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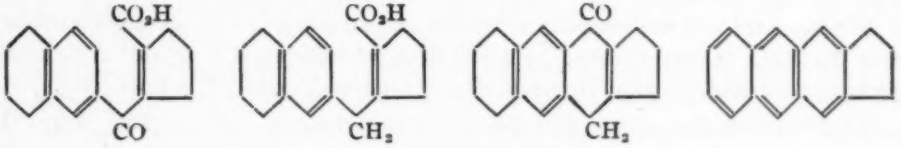
[Jour. Indian Chem. Soc., Vol. 30, No. 12, 1953]

SYNTHESIS OF POLYNUCLEAR HYDROCARBONS WITH FUSED *cyclo*PENTANE RING. PART II

By Suresh Chandra Sen Gupta and Anathjiban Bhattacharjee

The synthesis of 2:3-*cyclo*pentenoanthracene and 2:3:6:7-di*cyclo*pentenonaphthalene have been described.

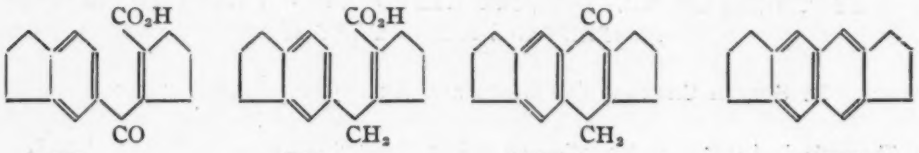
The method developed in Part I of this series (Sen Gupta and Saha, this *Journal*, 1952, **29**, 331) for the synthesis of polynuclear hydrocarbons with fused *cyclo*pentane ring has been extended in this communication. The synthesis of 2:3-*cyclo*pentenoanthracene has been carried out in the following manner. The anhydride of Δ^1-*cyclo*pentene-1:2-dicarboxylic acid condensed with tetralin in nitrobenzene solution in the presence of anhydrous aluminium chloride with the formation of Δ^1-*cyclo*pentene-1-(2′-tetroyl)-2-carboxylic acid (I), the orientation of tetralin in Friedel-Craft's reaction being exclusively at the unhindered β-position. This keto-acid on reduction by the Clemmensen method gave Δ^1-*cyclo*pentene-1-(2′-tetralylmethyl)-2-carboxylic acid (II) which was cyclised by heating with 85% sulphuric acid on a steam-bath to 1-keto-2:3-*cyclo*penteno-1:4:5:6:7:8-hexahydroanthracene (III). The cyclic ketone on the Clemmensen reduction gave 2:3-*cyclo*penteno-1:4:5:6:7:8-hexahydroanthracene. The latter on dehydrogenation with selenium at 280°-320° gave 2:3-*cyclo*pentenoanthracene or *lin*-hydrindanthracene (IV). The formation of this hydrocarbon proved that the expected linear cyclisation of the acid (II) had taken place.



(I) (II) (III) (IV)

Following a similar procedure, 2:3:6:7-di*cyclo*pentenonaphthalene (VIII) has been synthesised starting from hydrindene and Δ^1-*cyclo*pentene-1:2-dicarboxylic anhydride. These two condensed with the formation of Δ^1-*cyclo*pentene-1-(5′-hydrindoyl)-2-carboxylic acid (V). The constitution of the keto-acid follows from its oxidation with alkaline permanganate to trimellitic ac[illegible]. This keto-acid on reduction by the Clemmensen method gave Δ^1-*cyclo*pentene-1-(5′-hydrindylmethyl)-2-carboxylic acid (VI), which on cyclisation with 85% sulphuric acid gave 1-keto-2:3:6:7-di*cyclo*penteno-1:4-dihydronaphthalene (VII). The formation of this linear cyclisation product was proved by the formation of pyromellitic acid on oxidation of this cyclic ketone. A similar linear cyclisation of γ-5-hydrindylbutyric acid was noted in an earlier paper (Sen Gupta, this *Journal*, 1939, **16**, 89). The keto compound (VII) on the Clemmensen reduction gave

2:3:6:7-di*cyclo*penteno-1:4-dihydronaphthalene, which on dehydrogenation with selenium gave 2:3:6:7-di*cyclo*pentenonaphthalene (VIII). It was obtained as flakes, m.p. 183°, and readily formed a picrate.



(V) (VI) (VII) (VIII)

EXPERIMENTAL

Δ^1-cyclo*Pentene*-1-(2′-*tetroyl*)-2-*carboxylic Acid* (I).—A mixture of the anhydride of Δ^1-*cyclo*pentene-1:2-dicarboxylic acid (22 g.) and tetralin (27 g.) was added to a cooled solution of anhydrous aluminium chloride (54 g.) in nitrobenzene (150 c.c.). After standing for 16 hours the mixture was treated with ice and hydrochloric acid and nitrobenzene was removed by steam distillation. The solid product was extracted with hot sodium carbonate solution and the keto-acid was precipitated with hydrochloric acid. It was first crystallised from glacial acetic acid and then from rectified spirit, m.p. 178°, yield 25 g. (Found: C, 75.32; H, 6.79. $C_{17}H_{18}O_3$ requires C, 75.55; H, 6.66 per cent).

The *semicarbazone* of this keto-acid crystallised from rectified spirit, m.p. 230°. (Found: C, 65.9; H, 6.6. $C_{18}H_{21}O_3N_3$ requires C, 66.05; H, 6.42 per cent).

Δ^1-cyclo*Pentene*-1-(2′-*tetralylmethyl*)-2-*carboxylic Acid* (II).—The keto-acid (I, 22 g.), amalgamated zinc (90 g.) and concentrated hydrochloric acid (90 c.c.) were boiled gently for 24 hours. The reduced acid was extracted with ether, the ether removed, the residue extracted with hot sodium carbonate solution and acidified with hydrochloric acid. The separated acid was extracted with ether and after drying with magnesium sulphate was distilled. It was obtained as a very thick colorless liquid, b.p. 210°-213°/4 mm., yield 18 g. (Found: C, 79.3; H, 7.9. $C_{17}H_{20}O_2$ requires C, 79.68; H, 7.8 per cent).

1-*Keto*-2:3-cyclo*penteno*-1:4:5:6:7:8-*hexahydroanthracene* (III).—The acid (II, 14 g.) was heated with 85% sulphuric acid (56 c.c.) on a steam-bath for 1½ hours with stirring. The product was poured on crushed ice, extracted with ether, washed with ammonium hydrate, dried over magnesium sulphate and distilled. It is a colorless liquid with a characteristic odour, b.p. 190°-195°/4 mm., yield 9 g. It solidified on long standing and crystallised from petroleum ether (b.p. 40°-60°) in needles m.p. 116-17°. (Found: C, 85.4; H, 7.7. $C_{17}H_{18}O$ requires C, 85.7; H, 7.56 per cent).

The *oxime* of the ketone (III) was obtained by heating on a water-bath a solution of the ketone (1 g.), hydroxylamine hydrochloride (1 g.) and pyridine (10 c.c.) for 6 hours. The mixture was treated with water, filtered and the oxime crystallised from rectified spirit in needles, m.p. 151°. (Found: C, 80.53; H, 7.6. $C_{17}H_{19}ON$ requires C, 80.63; H, 7.5 per cent).

2:3-cyclo*Penteno*-1:4:5:6:7:8-*hexahydroanthracene*.—The cyclic ketone (III, 8 g.), amalgamated zinc (30 g.) and hydrochloric acid (30 c.c., conc.) were boiled for 24 hours,

The product was extracted with ether, dried and distilled under reduced pressure. The solid distillate was crystallised from methyl alcohol in needles, m.p. 96°. (Found: C, 90.7; H, 9.2. $C_{17}H_{20}$ requires C, 91.07; H, 8.92 per cent).

2:3-cyclo*Pentenoanthracene* or lin-*Hydrindanthracene* (IV).—The foregoing hydrocarbon (1.7 g.) and selenium (3 g.) were heated in a metal bath at 280°-290° for 8 hours and at 300°-320° for 16 hours. The product was extracted with hot benzene and distilled over sodium under reduced pressure. The solid distillate crystallised from benzene in flakes, m.p. 242-43° (lit. m.p. 242-43°). * (Found: C, 92.85; H, 6.48. Calc. for $C_{17}H_{14}$: C, 93.57; H, 6.42 per cent).

Δ^1-cyclo-*Pentene*-1-(5′-*hydrindoyl*)-2-*carboxylic Acid* (V) was prepared from hydrindene (26 g.), anhydride of Δ^1-*cyclo*pentene-1:2-dicarboxylic acid (37 g.) and aluminium chloride (54 g.), dissolved in nitrobenzene (150 c.c.), exactly as in the preparation of the keto-acid (I). It crystallised from rectified spirit in flakes, m.p. 187°, yield 40 g. (Found: C, 74.6; H, 6.2. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.1 per cent).

The *semicarbazone* was crystallised from rectified spirit, m.p. 254°. (Found: C, 64.95; H, 6.2. $C_{17}H_{19}O_3N_3$ requires C, 65.14; H, 6.07 per cent).

Oxidation of the keto-acid (V) was carried out by heating with an excess of alkaline permanganate solution on a steam-bath. The excess permanganate was destroyed with alcohol, the alkaline solution filtered, the filtrate acidified with hydrochloric acid and evaporated to dryness. The solid residue was extracted with ether and after evaporation of the solvent, the residue was crystallised from concentrated hydrochloric acid in white granules, m.p. 214° (decomp.). Mixed m.p. with a sample of trimellitic acid was unaltered.

Δ^1-cyclo*Pentene*-1-(5′-*hydrindylmethyl*)-2-*carboxylic Acid* (VI).—The keto-acid (V, 32 g.), amalgamated zinc (128 g.) and hydrochloric acid (conc., 130 c.c.) were gently boiled for 24 hours. The reduced acid was purified as in the case of the acid (II). It is a colorless, very thick liquid, b.p. 205°/5 mm., yield 27 g. (Found: C, 78.8; H, 7.7. $C_{16}H_{18}O_2$ requires C, 79.33; H, 7.43 per cent).

1-*Keto*-2:3:6:7-*di*cyclo*penteno*-1:4-*dihydronaphthalene* (VII).—The acid (VI, 22 g.) was heated for 1½ hours with 85% sulphuric acid (88 c.c.) on a steam-bath with stirring. The cyclised ketone was purified as in the case of (III). It was obtained as a colorless liquid, b.p. 195°/5 mm., and slowly solidified after a few days. It was crystallised from petroleum ether (b.p. 40°-60°) in stout needles, m.p. 116-18°, yield 14 g. (Found: C, 85.5; H, 7.3. $C_{16}H_{16}O$ requires C, 85.71; H, 7.14 per cent).

The *oxime* of ketone (VII) was prepared in pyridine solution. It crystallised from rectified spirit in needles, m.p. 161°. (Found: C, 79.55; H, 7.73. $C_{16}H_{17}ON$ requires, C, 80.3; H. 7.1 per cent).

Oxidation of Ketone (VII).—The ketone was heated on a water-bath with an excess of alkaline permanganate solution and the oxidation was finally completed by gentle boiling. The excess of $KMnO_4$ was removed with alcohol, the solution filtered, the filtrate evaporated to a small bulk, and acidified with hydrochloric acid. From this solution the polybasic acid formed was purified through its barium salt according to Read and Purves (*J. Amer. Chem. Soc.*, 1952, **74**, 118). The anhydride of the acid had m.p. 281° (mixed m.p. with a sample of dianhydride of pyromellitic acid was unaltered).

2:3:6:7-*Dicyclopenteno*-1:4-*dihydronaphthalene*.—The ketone (VII, 12 g.), amalgamated zinc (48 g.) and hydrochloric acid (conc., 48 c.c.) were boiled for 24 hours. The product was extracted with ether, washed with water, dried and distilled under reduced pressure. The solid distillate was crystallised from petroleum ether (b.p. 40°-60°), m.p. 128-29°. (Found: C, 91.1; H, 8.7. $C_{16}H_{16}$ requires C, 91.43; H, 8.57 per cent).

2:3:6:7-*Dicyclopentenonaphthalene* (VIII).—The foregoing hydrocarbon (2.5 g.) was heated with selenium (5 g.) at 280°-290° for 12 hours and at 300°-320° for 12 hours. The product was extracted with hot benzene, the solvent removed and the residue was distilled over sodium under reduced pressure. The solid distillate was converted into its picrate in benzene solution; the picrate was recrystallised from benzene in orange needles, m.p. 177°. * (Found: C, 60.56; H, 4.16. $C_{22}H_{19}O_7N_3$ requires C, 60.4; H, 4.34 per cent). The hydrocarbon was regenerated from the picrate and was crystallised from rectified spirit in flakes, m.p. 183°. * (Found: C, 92.13; H, 7.73. $C_{16}H_{16}$ requires C, 92.3; H, 7.69 per cent).

Microanalyses marked with an asterisk were carried out by Drs. Weiler and Strauss of Oxford.

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BEHAVIOUR OF FLUORINATED OLEFINES TOWARDS ANIONIC REAGENTS

By Albert L. Henne and Kazi Abdul Latif

The reactions of $CF_3CCl{=}CClCF_3$ and *cyclo*-$C_5F_6Cl_2$ were studied with methanol, ethylene glycol, malonic ester, $-OH^-$, $-CN^-$ and CH_3COO^-, all of them under basic conditions. Of these, the last three did not react at all, whereas very consistent results were obtained in the reaction with methanol and ethylene glycol, but the reaction of malonic ester was not very clear cut.

Vinylic substituted monoethers as well as products by further substitution in the allylic position were obtained from both of the above fluorochloro olefines. But in contrast to the monoether from *cyclo*-$C_5F_6Cl_2$, that from $CF_3CCl{=}CClCF_3$ gave also products by addition across the double bond.

Analysis and physical constants of all the new compounds have been given.

It is known that perfluoro*cyclo*butene (*cyclo*-C_4F_8) reacts with alcohols under basic condition to yield generally *cyclo*-$C_4F_4(OR)_2$, a vinylic substituted diether (Park, Sarrah and Lacher, *J. Amer. Chem. Soc.*, 1949, **71**, 2337), and under controlled conditions *cyclo*-$C_4F_5(OR)$, a vinylic monoether (Rapp *et al.*, *ibid.*, 1950, **72**, 4480). On the other hand, 1:2-dichloro-3:3′:4:4′-tetrafluoro-1-*cyclo*butene (*cyclo*-$C_4F_4Cl_2$) reacts with alcohols in presence of a base, to yield either a cyclic monoether of the formula, $C_4F_4Cl(OR)$ or a cyclic triether of the formula $C_4F_2Cl(OR)_3$, but no diether (Park *et al.*, *ibid.*, 1951, **73**, 2342).

To obtain a better idea of the apparent anomalous behaviour of fluorochloro and perfluoro olefines, it was intended to study both straight chain and cyclic compounds of each class. Also, instead of only one class of bases, different types of bases were employed. In this paper is described the behaviour of *cyclo*-$C_5F_6Cl_2$ and $CF_3CCl{=}CClCF_3$ towards a few anionic reagents and the relevant investigations on perfluoro olefines are in progress. The base was always added to the olefine and rarely otherwise, so that the influence of the former could be ascertained.

The various reagents that have been studied are $\bar{O}CH_3$, $\bar{O}CH_2CH_2OH$, $^-CH(COOEt)_2$, CN^-, OH^- and CH_3COO^-. Of these, the results obtained from the first two were quite consistent, while there was no reaction with the last three, and the reaction with sodium derivative of malonic ester was not very clear cut.

When *cyclo*-$C_5F_6Cl_2$ was treated with methanolic KOH solution, the results obtained were in line with those obtained from *cyclo*-$C_4F_4Cl_2$ (*loc. cit.*). By using one equivalent of the base, the product was *cyclo*-$C_5F_6Cl(OCH_3)$ and with two equivalents, this monoether was accompanied by a triether, *cyclo*-$C_5F_4Cl(OCH_3)_3$. But with $CF_3CCl{=}CClCF_3$, the results obtained were different. With one equivalent, the product was $CF_3CCl{=}C(OCH_3)CF_3$ as expected, but with two equivalents of the base, the products were $CF_3CHClC(OCH_3)_2CF_3$ and $CF_3CCl{=}C(OCH_3)CF(OCH_3)_2$, and no monoether. The relative amounts of the two were found to be dependent on temperature of the reaction and concentration of the base, a higher temperature and concentration favouring the formation of the latter. With three equivalents of the base, the entire product

was the triether. This would suggest that both $CF_3CCl=C(OCH_3)CF_3$ and $CF_3CHClC(OCH_3)_2CF_3$ might be the intermediates in the formation of $CF_3CCl=C(OCH_3)CF(OCH_3)_2$. Actually that was found to be the case because, when $CF_3CCl=C(OCH_3)CF_3$ was treated with methanolic KOH, both $CF_3CHClC(OCH_3)_2CF_3$ and $CF_3CCl=C(OCH_3)CF(OCH_3)_2$ were obtained, and when $CF_3CHClC(OCH_3)_2CF_3$ was treated separately with the same base, the conversion to $CF_3CCl=C(OCH_3)CF(OCH_3)_2$ was almost complete. From these observations, the following course of reaction is suggested for the formation of the above compounds:

$$\underset{(I)}{CF_3CCl=CClCF_3} \xrightarrow{CH_3OH} \underset{(II)}{[CF_3CHClC(OCH_3)ClCF_3]}$$

$$\downarrow -HCl$$

$$\underset{(V)}{CF_3CCl=C(OCH_3)CF(OCH_3)_2} \xleftarrow{\bar{O}CH_3} \underset{(III)}{CF_3CCl=C(OCH_3)CF_3}$$

$$\uparrow\downarrow CH_3OH$$

$$\underset{(IV)}{CF_3CHClC(OCH_3)_2CF_3}$$

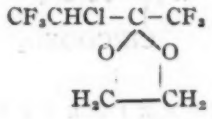
Here an addition-elimination mechanism has been suggested for the formation of $CF_3CCl=C(OCH_3)CF_3$. This is in accordance with the observation of Rapp and coworkers, who isolated an intermediate addition product from perfluoro*cyclo*butene and mercaptan (*ibid.*, 1950, **72**, 3642). Also, the formation and isolation of (IV) may be regarded as an indirect evidence for this mechanism, because if $CF_3CCl=C(OCH_3)CF_3$ can add one mole of alcohol, it is very likely that $CF_3CCl=CClCF_3$ will do the same thing with the formation of the intermediate unstable compound (II), which will then eliminate HCl under the basic conditions of the reaction. When compound (III) is formed, it can react in two ways to form either (IV) or (V) depending on conditions. The formation of (IV) is a reversible reaction, while that of (V) is irreversible. Higher temperature and concentration will favour the formation of the allylic substitution product (V), and hence, the equilibrium will be shifted. This view is further supported by the conversion of (IV) into (V) under proper conditions.

The product anologous to $CF_3CHClC(OCH_3)_2CF_3$ could not be isolated from *cyclo*-$C_5F_6Cl_2$ even at a low temperature and concentration. The explanation may be found in the fact that *cyclo*-$C_5F_6Cl(OCH_3)$ will always have a *cis*-configuration and like the mechanism of many addition reactions, probably a *trans*-configuration is needed for addition. Moreover, by making a model of the possible addition product, it is found that H and $-OCH_3$ are always in the *trans*-position, thus favouring elimination.

The structure for $CF_3CHClC(OCH_3)_2CF_3$ was established from analysis and also infra-red spectrum in which no double bond absorption band was present. The structure for $CF_3CCl=C(OCH_3)CF(OCH_3)_2$ was established through analysis and also oxidation with alkaline $KMnO_4$ solution, when CF_3COOH was found in the oxidation product and identified through the formation of its amide. That leaves choice between two possible structures only : (*a*) $CF_3CCl=C(OCH_3)CF(OCH_3)_2$ and (*b*) $CF_3C(OCH_3)=CClCF(OCH_3)_2$. Of these, the former is more likely, because intro-

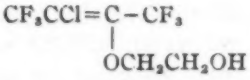
duction of $-OCH_3$ group into the vinylic position will make its nearest allylic atom more reactive towards substitution.

The reaction with ethylene glycol as its monosodium derivative was also consistent. Using one equivalent of the base, the following product was obtained from $CF_3CCl=CClCF_3$:



(VI)

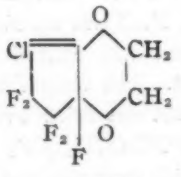
The first product to be expected will be



This contains one alcoholic function and thus is equivalent to one molecule of a monohydric alcohol. Under the basic condition of the reaction, a five-membered ring compound can be formed by addition across the double bond, and hence, the above ring compound is formed which is analogous to $CF_3CHClC(OCH_3)_2CF_3$. This was supported by the infra-red spectrum which did not show the presence of any $-OH$ group.

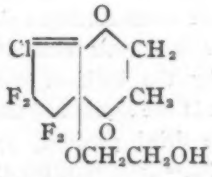
There was also a small amount of a higher boiling fraction which could not be obtained in pure form.

The following two products were isolated from the reaction of *cyclo*-$C_5F_6Cl_2$ with monosodium derivative of ethylene glycol:



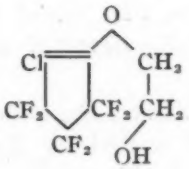
(VII)

and



(VIII)

and no product like



This is quite justifiable, because the latter has one free $-OH$ group, and hence, can replace one fluorine atom from the allylic position, provided that the solution is basic. So, the product is (VII). Now (VII) can react further with ethylene glycol to afford (VIII). This latter compound is the analogue of $CF_3CCl=C(OCH_3)CF(OCH_3)_2$. The structures for both (VII) and (VIII) were established from analysis and infra-red spectrum.

The reaction of monosodium derivative of malonic ester with either $CF_3CCl=CClCF_3$ or *cyclo*-$C_5F_6Cl_2$ was not very satisfactory, because this reaction was always accompanied by an intense coloration and tar formation. No clear cut product could be isolated, except from $CF_3CCl=CClCF_3$, when

$$\begin{array}{l} CF_3C=CClCF_3 \\ \quad\quad | \\ \quad\quad CH(COOEt)_2 \end{array}$$

was isolated and identified.

Experimental

cyclo-$C_5F_6Cl_2$ was prepared by the action of SbF_3, containing 10% SbF_3Cl_2, on *cyclo*-C_5Cl_6, by a slight modification of the process of Henne and Zimmerschied (*J. Amer. Chem. Soc.*, 1945, **67**, 1235). $CF_3CCl=CClCF_3$ was prepared by the method of Henne and Trott (*ibid.*, 1947, **69**, 1820) by the action of SbF_3Cl_2 on hexachlorobutadiene.

Reaction with Methanolic KOH.—The following typical example will illustrate the procedure usually followed:

$CF_3CCl=CClCF_3$ (117 g., 0.5*M*), dissolved in methanol (90 ml.), was taken in a three necked (500 ml.) flask provided with a mechanical stirrer, an addition funnel and a reflux condenser. A thermometer was inserted from the top of the condenser touching the liquid surface for measuring the temperature of the reaction. KOH (56 g., 1 *M*), dissolved in 210 ml. of methanol was added dropwise from the addition funnel at such a rate that a temperature of $45° \pm 2°$ was maintained (the reaction being exothermic). At the end of the reaction, an excess of water was added and a clear reaction product settled at the bottom, with some emulsion above it. Enough NaCl was added to break the emulsion. The clear liquid was taken off and the emulsion was filtered through anhydrous Na_2SO_4 whereby the bulk of water was absorbed. The clear filtrate was added to the main bulk of the liquid and the combined product was dried over P_2O_5. On fractionation of the dried product, 57.8 g. of $CF_3CHClC(OCH_3)_2CF_3$ (44.5% yield) and 42.5 g. of $CF_3CCl=C(OCH_3)CF(OCH_3)_2$ (33.7% yield) were obtained.

All other experiments with methanol, using either *cyclo*-$C_5F_6Cl_2$, $CF_3CCl=CClCF_3$, or any other product derived from them, were carried out in the same way only by changing, wherever necessary, the relative amount of reactants and the temperature and concentration of the base.

Reaction with Ethylene Glycol.—This reaction was carried out by using the monosodium derivative of ethylene glycol as the base. Ethylene glycol (200 g.) was taken into a 250 ml. three-necked flask, fitted with a reflux condenser through the middle neck, one inlet tube through one of the side necks, the other neck being closed by a stopper. Dry nitrogen gas was passed through the inlet tube so that there was an inert atmosphere inside the flask. Metallic sodium (11.5 g.), cut into fine pieces, was added one by one while the liquid was stirred with a magnetic stirrer. The first few pieces reacted very slowly, but after a while the rate of reaction increased. When the addition was completed, the solution was allowed to cool down.

2—1831P—12

TABLE I

New compounds.

Compound.	B.p.	n_D^{20}.	d_4^t.	M.R.	A.R$_F$	% Fluorine. Calc.	% Fluorine. Found.	% Chlorine. Calc.	% Chlorine. Found.
CF_2—CF_2—CF_2—C(OMe)=CCl	130° (742 mm.)	1.3750	1.5645 (27.4°)	34.9	1.29	.....	.....	14.76	14.74
CF_2—CF_2—C(OMe)$_2$—C(OMe)=CCl	100-101.5° (16)	1.4220	1.4291 (29°)	46.7	1.20	28.73	26.37	13.42	13.15
CF_3—CCl=C(OMe)—CF_3	84-85° (745)	1.3370	1.4703 (31°)	31.8	1.17	.....	.....	15.52	16.20
CF_3—CHCl—C(OMe)$_2$—CF_3	141-42° (747)	1.3560	1.4854 (31°)	37.9	1.05	43.8	42.79	13.62	13.65
CF_3—CCl=C(OMe)CF(OMe)$_2$	72°/6 mm.	1.3985	1.3965 (30°)	43.3	1.12	30.1	29.66	14.02	13.80
(VI)	85°/48	1.3630	1.5920 (29°)	35.82	1.09	44.1	42.84	13.72	13.44
(VII)	98°/53	1.3993	1.5760 (27.5°)	38.35	1.04	37.96	37.31	14.16	13.33
(VIII)	136-42° (2-3 mm.)	1.4508	1.5460 (29°)	50.60	1.19	26.0	25.64	12.12	12.04
CF_3—C(CH(CO$_2$Et)$_2$)=CCl—CF_3	80-82°/1	1.4018	1.3659 (29°)	63.00	1.50	31.97	28.44	9.95	9.90

$CF_2CCl{=}CClCF_3$ (118 g., 0.5 *M*), dissolved in 200 ml. of dioxane, was taken in an one litre three-necked flask with the usual arrangements. Dioxane was used as a common solvent for both ethylene glycol and $CF_2CCl{=}CClCF_3$. The base was added to the olefine. The rest of the procedure was the same as used in the case of methanol.

The reaction with *cyclo*-$C_3F_6Cl_2$ was also carried out in the same way.

Reaction with Malonic Ester.—In this case, the monosodium derivative of malonic ester was used as the base. The sodium derivative was prepared by adding requisite amount of sodium to malonic ester. Excess of malonic ester was also used as a common solvent for both the base and the olefine. The rest of the reaction was carried out as usual.

Reaction with CN^-, OH^- *and* CH_3COO^-.—The action of these bases were tried using KCN dissolved in CH_3OH, KOH dissolved in aqueous dioxane, and sodium acetate, dissolved in glacial acetic acid.

Oxidation of $CF_2CCl{=}C(OCH_3)CF(OCH_3)_2$.—Potassium permanganate (90 g.), KOH (40 g.) and water (175 ml.) were put into a three-necked (250 ml.) flask provided with a mechanical stirrer, an addition funnel and a reflux condenser, the top of the condenser being joined to a dry ice trap. $CF_2CCl{=}C(OCH_3)CF(OCH_3)_2$ (25.2 g.) was added dropwise to the refluxing solution. After several hours, the permanganate was all used up, and hence, 35 g. more of $KMnO_4$ and 10 g. more of KOH were added to the solution and the oxidation was allowed to go continuously for five days, at the end of which no more organic liquid was found refluxing, and hence, the reaction was stopped. It was then cooled and filtered from MnO_2 by suction, washing the MnO_2 several times with water. SO_2 was then passed through the pink solution till colorless.

H_2SO_4 (conc., 137.2 g.) and 95% ethanol (116 ml.) were added to this aqueous solution and then distilled through an efficient fractionating column. This was the method of making trifluoroacetate from an aqueous solution of trifluoroacetic acid (cf. Reid, *J. Amer. Chem. Soc.*, 1947, **69**, 2069).

First of all an azeotrope of trifluoroacetate, alcohol and H_2O came out at 54°, the temperature rising gradually to 78° as the mixture was taken out continuously. The distillation was carried out till the n_D value of the distillate was the same as that of 95% alcohol. The entire distillate was then added to ice-cold water, at which a lower layer of ester separated and was collected and dried over anhydrous $MgSO_4$. This ester was then suspended in dry ether and ammonia was passed for five hours, cooling the liquid in ice. The ether was then taken off completely under suction at which the amide crystallised out. It was then recrystallised from chloroform as beautiful crystals, m.p. 73-74°; mixed m.p. with an authentic sample of CF_3CONH_2 was also 73-74°. Hence, the presence of CF_3COOH in the oxidation mixture was confirmed.

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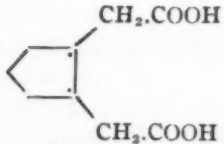
AZULENES AND RELATED SUBSTANCES. PART IV. PREPARATION OF *cis-cyclo*PENTANE-1 : 2-DIACETIC ACID

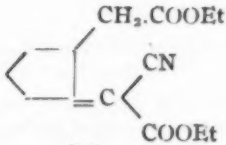
By Sukh Dev

Various steps in the preparation of *cis-cyclo*pentane-1 : 2-diacetic acid have been re-examined and improved overall yields obtained.

In some projected work on azulenes, relatively large amounts of *cis-cyclo*pentane-1:2-diacetic acid (I) were required (cf. Sörm and Fajkos, *Col. Czech. Chem. Comm.*, 1947, **12**, 81; Plattner and Studer, *Helv. Chim. Acta*, 1946, **29**, 1432). The intermediate, ethyl *cyclo*pentylidene-cyanoacetate-2-acetate (II) is available according to the method of Linstead and Meade (*J. Chem. Soc.*, 1934, 935; cf. Barret and Linstead, *ibid.*, 1935, 436) in an overall yield of about 20% starting from ethyl *cyclo*pentanone-2-carboxylate. However, when the preparation is carried out according to the procedures described in this communication, yields of over 67% can readily be obtained.



(I)



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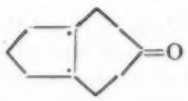

(III)

Ethyl *cyclo*pentanone-2-acetate (Kotz, *Annalen*, 1906, **350**, 235 ; Linstead and Meade, *loc. cit.*) was prepared essentially by the method of the latter workers, except that it was advantageous to carry out the esterification of the crude *cyclo*pentanone-2-acetic acid azeotropically. The next step, viz., the condensation of ethyl *cyclo*pentanone-2-acetate with ethyl cyanoacetate required a considerable study. Barrett and Linstead (*loc. cit.*) obtained a yield of 41% of the condensation product by allowing the reactants to stand at room temperature for a period of 14 days in the presence of piperidine. Plattner and Studer (*loc. cit.*) carried out this reaction in refluxing benzene, the water formed being carried away by the entrainer. The reaction required for completion a period of 48 hours and afforded 70% yield. By employing benzylamine, "ethylbenzylamine" (*i.e.*, not freed from traces of benzylamine) or piperidine-benzylamine mixture as catalysts (Sukh Dev, this *Journal*, 1953, **30**, 443, 665) a much improved yield of the desired material was obtained in a comparatively short period. Table I shows the results in a comparable manner.

The reduction of the unsaturated condensation product is best carried out catalytically (cf. Barett and Linstead, *loc. cit.*, who report the catalytic hydrogenation over Adam's catalyst as generally ineffective and prefer to carry out the reduction with aluminium amalgam, affording consistent yields of 75%). If the once distilled material is utilised for hydrogenation over Adam's platinum oxide catalyst, the results may be

erratic. However, if just prior to hydrogenation, the once-distilled material is refractionated, the catalytic reduction occurs smoothly and the dihydro product can be easily isolated in 90-95% yield. The nature of the catalyst also appears to have an effect on the yield of the final *cis-cyclo*pentane-1:2-diacetic acid. In a single experiment using Pd-on-$CaCO_3$ catalyst (Busch, *Ber.*, 1916, **49**, 1063 ; 1929, **62**, 1458), the benzylamine catalyst condensation product after reduction, hydrolysis and decarboxylation gave a good yield of a mixture of *cis*- and *trans*-dibasic acids (m.p. 150°) from which it was very difficult to isolate pure *cis*-acid by fractional crystallisation (cf. Roberts and Gorham, *loc. cit.*). For the preparation of the *trans*-acid, thus, this catalyst appears to be advantageous; whereas for the *cis*-acid, Adam's platinum oxide catalyst must be used.

TABLE I

Ethyl cyclo*pentylidene-cyanoacetate-2-acetate* (II)*.

No.	Catalyst.	Time.	Yield.
1.	Piperidine †	31 hrs.	55 %
2.	Benzylamine	3-4	92
3.	"Ethylbenzylamine"	6	92
4.	Piperidine-benzylamine	6	90
5.	Ammonium acetate	15 ‡	68

* From 0.3 *M* of the keto-ester and 0.33 *M* of ethyl cyanoacetate, 0.03 *M* of the catalyst, 9 ml. of acetic acid and 75 ml. of benzene.

† Cf. Plattner and Studer, *loc. cit.*

‡ Data as given in a paper by Roberts and Gorham (*J. Amer. Chem. Soc.*, 1952, **74**, 2278). A prepublication copy was available to the author after this work had been completed.

The reduced ester on simultaneous hydrolysis and decarboxylation with dilute hydrochloric acid in acetic acid gives the required *cis-cyclo*pentane-1:2-diacetic acid together with other by-products like the *trans*-acid and the *cis*-bi*cyclo*-(0:3:3)-octanone (III).

In a number of cases it was observed that if benzylamine had been employed in the preparation of (II), the yields of the required acid were low and the bi*cyclo*ketone (III) was obtained in 9-13% yields. However, when piperidine or piperidine-benzylamine was the catalyst, the yield of the *cis*-acid was better. The condensation product (II), prepared by using either benzylamine or piperidine or piperidine-benzylamine, appeared to contain the various isomers in the same proportions, as in a comparative study the product from either source had the same physical properties (n^{24}, 1.4860; m.p. 30°, thermometer dipping in a 4″ layer of the compound in a test-tube and m.p. recorded just when the liquid became clear). At present it is not possible to explain this difference.

EXPERIMENTAL*

Ethyl cyclo*Pentanone-2-carboxylate.*—Diethyl adipate (606 g., 3 *M*; "Organic Synthesis", Vol. 17, p. 32) was cyclised by using powdered sodium (103.5 g., 4.5 g. atom) in pure benzene (2 litres) by the method of Linstead and Mead (*loc. cit.*). The product was

* All m.p. and b.p. uncorrected. For the calculation of M_D, data taken from Weissberger, "Tech. of Org Chem.", Vol. I, Part II, p. 163, 1949, New York. Measurements of vacuum by a vacustat.

well cooled in ice-salt bath and decomposed with dilute acetic acid (1:1, 1200 ml.). When all the sodium salt had disappeared (several hours at room temperature) the benzene layer was separated, washed with water (300 ml. × 2), $NaCO_3$ solution (10%, 300 ml. × 2) and finally again with water (300 ml.) and dried (Na_2SO_4); yield of the once-distilled (1 ft. Vigreux column) product, 85-88% ; b. p. 86°-87°/4 mm., n^{21}, 1.4515 (cf. "Organic Synthesis", Vol. 17, p. 30).

Ethyl cyclo*Pentanone-2-carboxylate-2-acetate*.—Sodium dust (28.75 g., 1.25 g. atom) in dry toluene (800 ml.) was treated with ethyl *cyclo*pentanone carboxylate (195 g., 1.25*M*) in three lots (15 minutes) with ice-cooling. As the reaction slowed down, it was allowed to stand at room temperature (28°) for half-an-hour and finally heated on the steam-bath for 3 hours with occasional swirling (silica gel guard-tube). The almost white sodium salt was well cooled in ice-water-slush and treated with ethyl chloroacetate (171.6 g., 149 ml., 1.4 *M*) in one lot and left overnight (15 hours) as such. The mixture was refluxed with occasional swirling for 5 hours in an oil-bath (140°-145°), cooled, diluted with water (600 ml.), and the toluene layer was separated and washed with water (100 ml. × 2). The combined aqueous parts were extracted once with toluene (100 ml.). The mixed toluene solutions were washed with water (200 ml.) and then with brine (250 ml. × 2). If necessary, a preliminary drying was carried out in the separating funnel by vigorously shaking with anhydrous Na_2SO_4 (20 g.) till it clarified and finally dried (Na_2SO_4) overnight. The solvent was fractionated off (12" Vigreux column) under vacuum (bath temperature not to exceed 150°) and the residue fractionally distilled to yield a colorless, mobile liquid, b. p. 134-35°/2 mm., 126°/0.9 mm., n^{23}, 1.4560—1.4550; yield 85-87%. For analytical purposes, a small central cut was refractionated, b. p. 128°/1.5 mm., n^{26}, 1.4540 ; d_4^{26}, 1.1117 ; M_D,58.94 (calc. for $C_{12}H_{18}O_3$: M_D, 58.74). Linstead and Meade (*loc. cit.*) give b.p. 150°-180°/22 mm.

Ethyl cyclo*Pentanone-2-acetate*.—The above ester (242 g., 1*M*) was mixed with water (242 ml.) and concentrated hydrochloric acid (484 ml.) and heated on a steam-bath. Evolution of CO_2 soon started and the reaction mixture became homogeneous in 1½ to 2 hours. Heating was continued for a total period of 12 hours, after which the excess aqueous acid was distilled off under vacuum (water-pump) from a metal-bath (140°-170°). The residue on cooling set to a crystalline cake. To this was added CCl_4 (50 ml.), which was distilled off later under reduced pressure to remove last traces of water. To the product, CCl_4 (100 ml.), alcohol (absolute, commercial; 130 ml.) and *p*-toluene sulphonic acid monohydrate (3 g.) were added and a continuous water separator attached (cf. Sukh Dev, *loc. cit.*) and gently refluxed till no more water separated (about 3 hours). Refluxing was continued for another ½ hour. The product was cooled, washed once with water (100 ml.), the washings extracted with CCl_4 (30 ml.) and mixed with the main solution. This after washing with $NaHCO_3$ solution (10%, 150 ml. × 1) was dried (Na_2SO_4). The solvent was flashed off (column) and the residue carefully fractionated. The keto-ester was obtained as a colorless, mobile liquid, b.p. 100°/3 mm., 105°/5 mm., n^{24}, 1.4516-1.4520; yield 88-90%. An analytical sample had n^{23}, 1.4515; d_4^{25}, 1.054; M_D, 43.44 (calc. for $C_9H_{14}O_3$: M_D, 43.23). Linstead and Mead (*loc. cit.*) give b.p. as 123°/13 mm.

2:4-*Dinitrophenylhydrazone* was prepared by the usual method (H_2SO_4) and after two crystallisations from alcohol furnished fine, yellow needles (can also be obtained as lustrous plates if the solution is concentrated), m. p. 107-108°. (Found: N, 16.2. $C_{15}H_{18}O_6N_4$ requires N, 16.0 per cent).

Ethyl cyclo*Pentylidene-cyanoacetate-2-acetate* (II).—The above keto-ester (136 g., 0.8 *M*), ethyl cyanoacetate (92.8 g., 0.82 *M*), piperidine (6.1 g., 0.072 *M*), benzylamine (0.86 g., 0.008 *M*), glacial acetic acid (15 ml.) and pure benzene (150 ml.) were mixed and gently refluxed with continuous removal of water (cf. Sukh Dev, *loc. cit.*). The separation of water practically stopped after 5 hours. The refluxing was continued for another hour during which period some benzene (about 70 ml.) was tapped off in order to remove last traces of moisture. The reaction mixture was cooled, diluted with ether (100 ml.) and washed with water (100 ml. × 2) and finally with brine (100 ml. × 2). After thorough drying (Na_2SO_4), the solvents were flashed off (column) and the residue fractionated. After a very small fore-run of unreacted materials, the product was obtained as a colorless, viscous liquid, b. p. 158°-160°/0.75 mm., 155°/0.5 mm., n^{24}, 1.4860 ; n^{29}, 1.4830 ; yield 90-92%. Linstead and Mead (*loc. cit.*) give b.p. as 180°-205°/5 mm., Plattner and Studer (*loc. cit.*) record the b.p. 168°-174°/0.5 mm.

Ethyl cyclo*Pentane-1-cyanoacetate-2-acetate*.—It has been found convenient to employ the following modification of Frampton, Edwards and Henze's method for the paeparation of Adam's platinum oxide catatyst (*J. Amer. Chem. Soc.*, 1951, **73**, 4432).

A solution of 4.5 g. of H_2PtCl_6 in the smallest amount of distilled water was mixed with potassium nitrate (20 g., A. R.) and the whole carefully evaporated to dryness to a powder Potassium nitrate (60 g., A.R.) was melted in a 400 c.c. pyrex beaker over a naked flame and just after melting heated for 5 minutes with the full blast of an ordinary burner. The dry powder was then introduced in three lots, the second addition being made as soon as the vigorous reaction due to the first addition was over. This took two minutes. Heating was continued at this temperature with stirring till the evolution of gas practically had stopped (10 minutes), and for another 5 minutes and the catalyst isolated in the usual manner; yield 95%. For maximum activity, the catalyst should be thoroughly dried for at least 24 hours in a vacuum desiccator.

In a typical hydrogenation experiment, the above unsaturated ester (100 g., redistilled), ethyl alcohol (80 ml., distilled over a little Raney nickel) and the PtO_2 catalyst (600 mg.) were shaken in an atmosphere of hydrogen in the usual manner. Hydrogenation came to a close after 4 hours when 100.1% of the theoretical amount of H_2 had been consumed. After filtering off the catalyst, the solvent was flashed off and the residue hydrolysed directly. The pure product may also be isolated in 94% yield by fractionating the residue under vacuum. It is a colorless, viscous liquid, b.p. 149°/0.5 mm., n^{25}, 1.4620 (cf. Linstead and Meade, *loc. cit.*).

In a single experiment usiug Pd-on-$CaCO_3$ catalyst (6 g. for 39 g. of the unsturated ester in 90 ml. of ethyl alcohol), the reduction was over after 6 hours. The product distilled at 149°/0.5 mm. and had n^{25}, 1.4630, yield 36 g. (cf. Roberts and Gorham, *loc. cit.*).

cis-cyclo*Pentane*-1:2-*diacetic Acid* (I).—In a typical experiment, the above reduced ester (equivalent to 90 g. of the unsaturated compound; undistilled), hydrochloric acid (C.P., 270 ml.), water (90 ml.) and acetic acid (90 ml.) were refluxed for 16 hours. The excess acids, etc., were distilled off, later (after about 175 ml. of the distillate had been collected) under vacuum (100-40 mm.) till due to the separated solids bumping of the residue became appreciable. The residue was cooled, diluted with water (200 ml.) and cautiously treated with solid sodium carbonate with slight warming till alkaline to litmus. This was extracted with ether to remove neutral materials. [The ethereal solution on removal of the solvent gave 13 g. of a dark oily product, consisting essentially of unhydrolysed ester and the nitrile (*trans*-: cf. Sörm and Fajkos, *loc. cit.*]. The sodium carbonate solution was saturated with salt, if necessary, and the p_H adjusted approximately to 5 and treated with norit. The clarified filtrate (practically colorless) was acidified to p_H 2 with concentrated hydrochloric acid, heated till clear and allowed to crystallise. After several hours at room temperature and 5 hours in the Frigidaire, the product was collected, m.p. 166-68° ; yield 28-30 g. One crystallisation from water (125 ml.) gave white silky needles, m.p. 169-70°; yield 25-27 g. Pure *cis-cyclo*pentane-1:2-diacetic acid (I) melts at 172-73°. The aqueous distillate was partially neutralised with solid sodium carbonate (caution) till an oil separated. This was taken up in petroleum ether (b. p. 40°-60°; 30 ml. × 2) washed with water and dried (Na_2SO_4). On working up it yielded the ketone (III) as a colorless, mobile liquid, b.p. 96°/25 mm., yield 5 0 g. Its 2:4-*dinitrophenylhydrazone* (HCl method) was obtained in yellow needles, m.p. 115-16° (Roberts and Gorham, *loc.cit.* give m.p. 115-16°).

All mother-liquors of the *cis*-acid (I) were combined and evaporated till appreciable amounts of solids separated out. This on ether extraction and working up in the usual manner yielded 15 g. of an oil, which completely crystallised out after 5 days at room temperature. These crude mixed acids were ketonised according to Barrett and Linstead (*loc. cit.*) to yield *cis*-ketone (III) (2 g.).

When the unsaturated ester (II) was reduced by Pd-on-$CaCO_3$ catalyst and then hydrolysed with dilute hydrochloric acid (HCl, 102 ml., water, 34 ml. for 34 g. of the reduced ester) and worked up as above, it gave a mixture of *cis*- and *trans*- acids (10.5 g.), m.p. 150°. From the melting-point-composition curve (Barrett and Linstead, *loc. cit.*) it should contain ~ 45% of the *trans*- and ~ 55% of the *cis*-diacid. After seven crystallisations from water it yielded 3 g. of the *cis*-acid (m.p. 167-68°).

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INDIGOID VAT DYES OF THE ISATIN SERIES. PART VII. 3-INDOLE-2′-(5′-BROMO)THIONAPHTHENE-INDIGOS

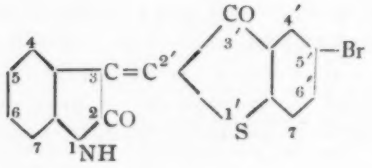
By Sisir Kumar Guha and Krishna Dulal Banerjee

3-Indole-, 3-(5-chloro)indole-, 3-(5-bromo)indole-, 3-(5:7-dibromo)indole-, 3-(5-bromo-7-nitro)indole-3-(5:7-dinitro)indole-2′-(5′-bromo)-thionaphthene-indigos have been prepared and the influence of bromine atom in 5′-position of the thionaphthere ring of Thionidigo Scarlet-R and its derivatives has been investigated with a view to studying together the gradational change in the colour of the dyestuffs due to the entrance of Me, Cl and Br in succession.

Although E.P. 313,493 described the condensation of α-chlorides of halogen isatins with 5-bromo-3-hydroxythionaphthene, thioindigoid dyes have not been hitherto prepared by the condensation of isatin and its important substituted products with the bromohydroxythionaphthene respectively.

In Parts I and V of the series (Guha and Basu Mallick, this *Journal*, 1934, **11**, 395; 1946, **23**, 214) the change in colour due to the successive introduction of a CH_3 group and a Cl atom in the 5′-position of the thionaphthene ring of Thioindigo Scarlet-R and its derivatives was studied.

In this communication the influence of a Br atom in the same 5′-position of the thionaphthene ring of Thioindigo Scarlet-R and its derivatives has been investigated with the object of studying together the gradational change in the colour of the dyestuffs due to the entrance of CH_3, Cl, and Br atom in succession. Therefore, 3-indole-, 3-(5-chloro)indole-, 3-(5-bromo)indole-, 3-(5:7-dibromo) indole-, 3-(5-bromo-7-nitro)indole-, 3-(5:7-dinitro)indole-2′-(5′-bromo)thionaphthene-indigos were prepared having the general constitutional formula (I).



(I)

These compounds of the 5′-bromo series are all violet-red crystalline products melting above 300°. They are soluble in aniline, nitrobenzene and tetraline. The violet-red solution of these dyes in tetralin, on continued boiling, turned light yellow which on standing regained the colour in the case of the first four substances mentioned above, but the yellow solution of the bromonitro and the dinitro compounds became brownish yellow only. They are sparingly soluble in alcohol and CCl_4. Except the parent compound and its dinitro derivative, the rest are sparingly soluble in acetic

acid, amyl alcohol and acetone. The mother substance, its bromonitro and the dinitro derivatives dissolve in cold strong sulphuric acid producing a blue solution, whereas the 5-chloro-, 5-bromo, and 5:7-dibromo compounds yield a light green solution when treated similarly. All the substances were reduced by alkaline sodium hydrosulphite at 50° to 60° into a yellow vat except the dinitro compound whose vat was deep yellow from which the shade developed on cotton were uniform, although not fully developed. The colour and the dyeing shades of some of the dyestuffs of this 5′-bromo series were compared with those of the corresponding substances of the 5′-methyl and 5′-chloro series. It is now concluded that the intensity of colour can be arranged in the order: 5′-bromo dyes> 5′-chloro dyes> 5′-methyl dyes (Table I).

5:5′-Dibromothioindigo (D.P. 225132) was described as reddish violet powder, obtained by brominating Thioindigo Red-B. Now it has been prepared in violet tufts of needles by the oxidation of a pure specimen of 5-bromo-3-hydroxythionaphthene by alkaline potassium ferricyanide in the usual way and crystallising from nitrobenzene, melting above 300°. This symmetrical dye resembles the asymmetrical dye, described in this paper, in solubility in aniline, nitrobenzene and tetraline. The beautiful violet-red tetralin solution of the substance on boiling for sometime also became yellow which remained the same even on standing for several days. The solution of this dye in cold strong sulphuric acid is light green.

TABLE I

T = Thionaphthene-indigo.

Compounds.	Dyeing shade on cotton.
3-Indole-2′- (5′-Me)-T	Red
3-Indole-2′- (5′-chloro)-T	Deep red
3-Indole-2′- (5′-bromo)-T	Violet-red
3-(5:7-Dibromo)indole-2′-(5′-Me)-T	Deep red
3-(5:7-Dibromo)indole-2′-(5′-chloro)-T	Violet-red (deeper shade)
3-(5:7-Dibromo)indole-2′-(5′-bromo)-T	Violet-red (Do)
3-(5:7-Dinitro)indole-2′(5′-Me)-T	Dark red
3-(5:7-Dinitro)indole-2′-(5′-chloro)-T	Deep violet-red
3-(5:7-Dinitro)indole-2′-(5′-bromo)-T	Dark violet

EXPERIMENTAL

The 3-indole-2′-(5′-bromo)thionaphthene-indigos, described in Table II, were prepared in the same way as 3-indole-2′-(5′-methyl)- and 3-indole-2′-(5′-chloro)-thionaphthene-indigos (*loc. cit.*) had been prepared. The glacial acetic acid solution of the reactants on treatment with 2 to 3 c.c. of strong HCl was boiled for 15 minutes only. The separated dyes were collected, washed with a little acetic acid and then with hot water and next crystallised from nitrobenzene, except the parent dye which was crystallised from xylene in beautiful crystals.

TABLE II

T = Thionaphthene-indigo. B = 5-bromo-3-hydroxythionaphthene.

Compound.	Formula.	Reactants.	Glacial acetic acid used and appearance.	Yield.	Solubility.	Dyeing shade on cotton.	Analysis Found.	Calc.
3′-Indole-2′-(5′-bromo)-T	$C_{16}H_8O_2NSBr$	Isatin (0.52 g.) + B (0.8 g.)	60 c.c., star-like clusters of needles.	0.867 g. (69%)	In pyridine and xylene; moderately in acetone, acetic acid, amyl alcohol.	Violet-red	N, 4.1	3.9
3-(5-Chloro) indole-2′-(5′-bromo)-T	$C_{16}H_7O_2NSClBr$	5-Chloroisatin (0.54 g.) + B (0.69 g.)	65 c.c., small clusters of needles.	0.91 g. (77%)	Moderately in pyridine; sparingly in xylene.	Do	N, 3.9	3.56
3-(5-Bromo) indole-2′-(5′-bromo)-T	$C_{16}H_7O_2NSBr_2$	5-Bromoisatin (0.68 g.) + B (0.69 g.)	70 c.c., long needles.	1.01 g. (77%)	Do	Do	N, 3.1	3.2
3-(5:7-Dibromo)-indole-2′-(5′-bromo)-T	$C_{16}H_6O_2NSBr_3$	5:7-Dibromoisatin (0.92 g.) + B (0.69 g.)	80 c.c., thread-like long needles.	1.38 g. (89%)	Moderately in pyridine and xylene.	Do	N, 3.0	2.7
3-(5-Bromo-7-nitro)-indole-2′-(5′-bromo)-T	$C_{16}H_6O_4N_2SBr_2$	5-Bromo-7-nitro-isatin (0.68 g.) + B (0.57 g.)	Do	1.02 g. (86%)	In pyridine: moderately in xylene.	Light violet-red.	N, 6.1	5.8
3-(5:7-Dinitro)-indole-2′-(5′-bromo)-T	$C_{16}H_6O_6N_3SBr$	5:7-Dinitroisatin (0.71 g.) + B (0.69 g.)	90 c.c., thread-like long needles.	1.09 g. (81%)	In pyridine; moderately in xylene, acetic acid, amyl alcohol, acetone.	Dark violet	N, 8.9	9.38
5:5′-Dibromo-thioindigo	$C_{16}H_6O_2Br_2S_2$	B (0.75 g.) in 50 c.c. dil. NaOH oxidised by 60 c.c. dil. $K_3Fe(CN)_6$.	Tufts of needles.	0.61 g. (82%)	Sparingly in xylene, acetic acid, acetone, amyl alcohol.	Pleasant bluish violet (cf. D.P. *loc. cit.*) (Bordeaux red).	Br, 34.8	35.24

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AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID CONTAINING GLUCOSE

By Hussein Sadek and Saad Eldin Zayan

When glucose is added to aqueous solutions of HCl (0.005, 0.05 *m*) tinted with thymol blue, the p_H value is lowered and the optical density increases linearly when the mole fraction of glucose is low. The results are interpreted by the aggregation of water molecules around glucose and by the electrostatic effects of the proton on the >O linkage. The results are expressed by the equation:

$$D = p_K - p_H - A\sqrt{m_{app}}.$$

Zhukov and Dneprov (*J. Gen. Chem. USSR.*, 1940, **10**, 291) investigated the effect of non-electrolytes such as sucrose on the electrical conductance and p_H values of aqueous hydrochloric acid solutions. They found that the transport number of the chloride ion remained constant in these solutions up to 30% sucrose by weight, while the p_H value decreased with the progressive addition of sucrose. However, Fisher and Koval (*Univ. Kiev Bull. Sci. rec. chim.*, 1939, **4**, 137) showed that sucrose, acetone or urea reduced the transport number of the hydrogen ion in aqueous sulphuric acid solutions. They concluded that complex ions of the type (H_3O^+, non-electrolyte) were formed. The experiments of Bartlett and Dauben (*J. Amer. Chem. Soc.*, 1940, **62**, 1339) showed that phenols increased the acid strength of hydrochloric acid in dioxane as a solvent. Their results were explained by the formation of hydrogen bond with the chloride ion by the hydroxyl group of the added phenol. In this paper, results on the increase of the hydrogen-ion concentration of hydrochloric acid by the addition of glucose in aqueous solution, as revealed by colorimetric and p_H value measurements, are reported.

Experimental

Hydrochloric acid solutions were always obtained by weight dilution of the constant boiling acid. The concentrations of the stock solutions were determined gravimetrically in triplicate as silver chloride; these agreed to ±0.02%. Anhydrous "Judex" glucose was used without further purification. The Spekker photoelectric absorptio meter (model H) was used for the measurement of the optical density of the acid solutions tinted by a few drops of thymol blue. The absorption spectra were obtained by the use of the Unicam absortptio meter (model S. P. 500). The p_H values of the solutions were measured by means of a Cambridge p_H meter with an accuracy of 0.02 of a p_H unit. All the measurements were carried out at 25°.

To investigate the relationship between the density of the transmitted light ($D = -\log I/I_o$) and the p_H values of aqueous hydrochloric acid solutions and of the same solutions containing progressively increasing amounts of glucose, the colorimetric method is most suited for this purpose because of its high sensitivity to small variations in the hydrogen-ion concentration. Accordingly use was made of the two-coloured indicator, thymol blue having a p_H range of 1.2-2.8 covering the p_H values of the acid solutions in the concentration range 0.005-0.06*m* (Lothian, *Trans. Faraday Soc.*, 1937, **33**, 1239).

To 25 c.c. of the acid solution 6 drops of thymol blue solution (B.D.H., CN 2067) were added and the optical density was measured in cells (4 cm. long) using water as a reference and filter No. 504.

Fig. 1 shows the relationship of the density of the transmitted light to the molality of the acid solutions containing no glucose. The curve obtained was employed to interpolate the molality of the HCl-glucose solutions from the measured optical density of these solutions. A plot of the apparent molality against the mole fraction of glucose gave straight lines with slopes decreasing from 0.5 to 0.26 as the initial concentration of pure HCl solutions decreased from 0.05 *m* to 0.005 *m*. In Fig. 2 the density of the transmitted light is plotted against the mole fraction of glucose. It can be seen that when the mole fraction of glucose is low, the relationship is linear but tends towards a constant value at high concentrations of glucose. This behavior is more marked in the concentrated than in the more dilute solutions of hydrochloric acid.

FIG. 1

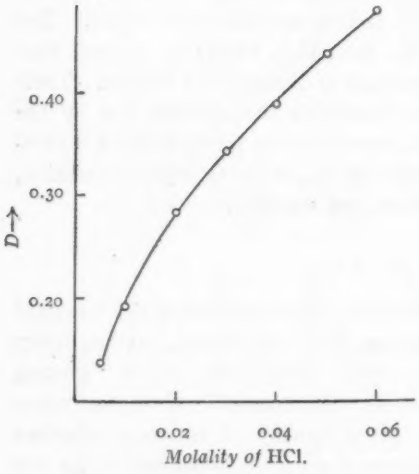
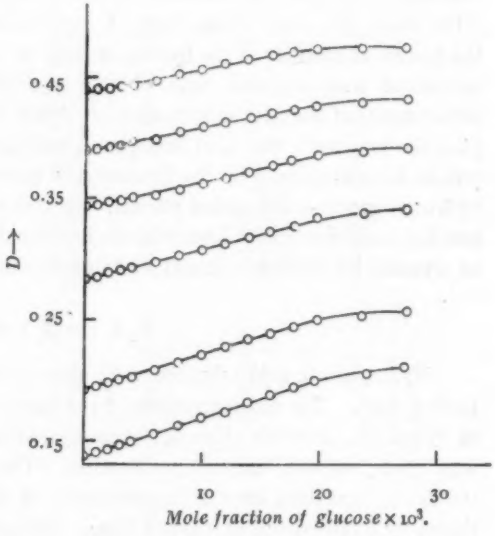


FIG. 2

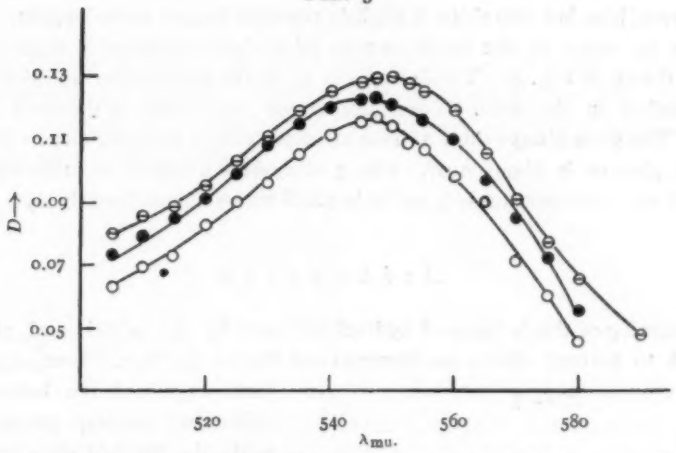


These data could be represented by the equation:

$$D - D_o = Abx/(1 + bx),$$

where D and D_o are the optical density of HCl- glucose solutions and pure HCl solutions respectively, x, the mole fraction of glucose and A and b are constants. Two limiting cases could be readily seen. If $bx \gg 1$, then $D - D_o = A$ = constant. Secondly, if $1 \gg bx$, then $D - D_o = Abx$, *i.e.*, D varies linearly with x. However, a plot of D against the square root of the apparent molality (m_{app}) of the acid in the presence of glucose gave a straight line passing through the origin with a slope equal to 2.

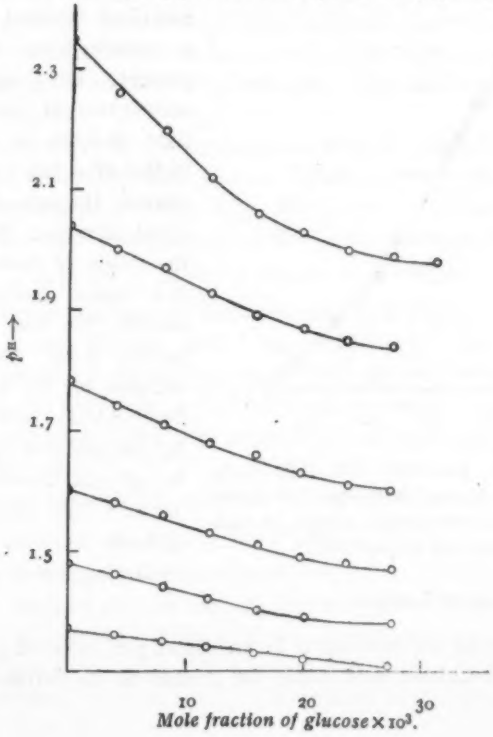
FIG. 3



Absorption spectra of pure hydrochloric acid (0.03 *m*) bottom curve; on the addition of 4 g. glucose per 50 c.c., (middle) ; and of 6 g. per 50 c.c. (top).

FIG. 4

Variation of p_H with mole fraction of glucose:

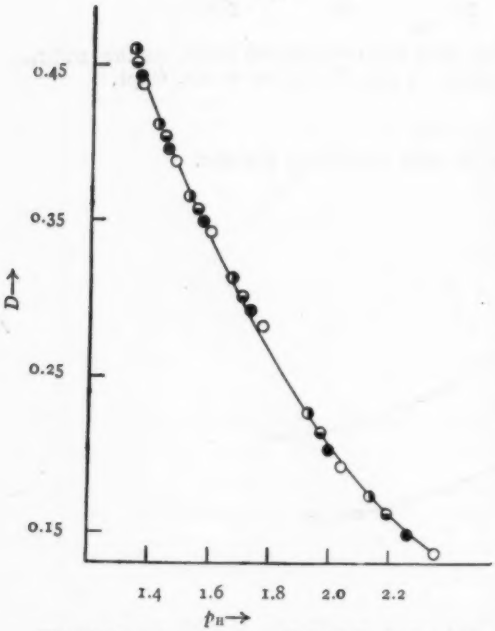


The addition of glucose to dilute HCl solutions not only broadens the absorption peak of thymol blue but also shifts it slightly towards longer wave-lengths. The variation of the p_H value of the solutions with increasing concentration of glucose (as mole fraction) is shown in Fig. 4. The decrease in p_H by the progressive addition of glucose is quite marked in the more dilute (uppermost curve) than in the more concentrated solutions. The plots always show a linear variation with a negative slope when the mole fraction of glucose is about 0.01. Fig. 5 represents a general relationship between D and p_H of all the solutions studied; up to p_H 1.8 D varies almost linearly with p_H.

DISCUSSION

The lowering of the p_H value of hydrochloric acid by the addition of glucose could be ascribed to solvent effects as Bancroft and Davies (*J. Phys. Chem.*, 1930, **34**, 2479) have explained the influence of boric acid on the rotatory power of tartaric acid. In the first place aggregation of water molecules around non-electrolytes was observed many years ago by Scatchard (*J. Amer. Chem. Soc.*, 1921, **43**, 2406) who showed that sucrose solutions behaved ideally even when a pentahydrate was assumed to be present. His theory was based on the assumption of the similarity of the field of force of a sucrose molecule to that of a water molecule, since both contain the same H and OH groups in equal number. Such a similarity in the fields of force will cause glucose and water molecules to congregate around the ions in solution. This picture lends itself to explain the increase of the ion-size parameter of hydrochloric acid from 4.3 to 6.6Å by the addition of glucose (Williams, Knight and Crockford, *ibid.*, 1950, **72**, 1277). This result indicates that a glucose molecule can enter into the hydration sheath of the ions and would thus replace few water molecules.

FIG. 5



The circle refers to pure HCl, full shade circle, horizontaly half-shaded and vertically half-shaded circles refer to solutions containing glucose at mole fractions 0.004, 0.008 and 0.012 respectively.

If n moles of water are assumed to be associated per mole of glucose, the apparent molality, m' of hydrochloric acid could be related to its initial molality (m) by the equation:

$$m' = \frac{1000\ m}{1000 - 18\ ny}$$

where y is the number of moles of glucose added to 1000 g. of water. The values of n in the various solutions are given in Table I. It can be readily seen that although the values of n are reasonable at concentrations of HCl above 0.02 m, they become unbelievably high in the more dilute solutions.

TABLE I

			m-HCl.			
18 y.	0.005.	0.01.	0.02.	0.03.	0 04.	0.05.
			Values of n.			
4	40.2	14.5	18.5	12.7	7.9	5.5
8	40.1	23.3	16.3	11.4	8.5	9.2
12	33.1	22.7	16.1	11.9	8.7	8.9
16	30.2	21.4	15.1	11.5	8.6	8.4

Therefore, congregation of water molecules around glucose cannot alone explain the observed increased acidity of hydrochloric acid.

Secondly, electrostatic action between the solvated proton and glucose enhances the shifting of electrons along the carbon chain towards the >O linkage, thus inducing a local positive charge ($\delta+$) on the hydrogen atom of the nearest OH group. The localisation of such a charge density on the glucose molecule is responsible in part for the observed increase in acidity. This effect is quite reasonable since glucose and most oxygen compounds, such as ethers, alcohols and ketones, show a great tendency to accept a proton from strongly acid solutions (Fredenhagen, Cadenbach and Klatt, *Z. physikal. Chem.*, 1933, **A164**, 176).

Our view is supported by the findings obtained from the catalytic effect of the hydrogen ions in the bromination of ketones, where a ketone-proton complex is formed as an intermediate (Bonhöffer and Reitz, *ibid.*, 1937, **A179**, 135). Furthermore, the hydrogen-ion catalysis of the mutarotation of glucose confirmed the existence of the equilibrium:

$$\text{Glucose} + H_3O^+ = [\text{glucose, H}]^+ + H_2O,$$

which involves ion-dipole interaction (Leininger and Kilpatrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2891; Amis and Holmes, *ibid.*, 1941, **63**, 2231). Also, infra-red spectra of tetramethylethylene glycol in the presence of dry HCl showed that the acid acted as an electron acceptor since the internally bonded band was weakened *because some of it* was converted into the polymeric OH, thus confirming our view of electrostatic action (Kuhn, *ibid.*, 1952, **74**, 2492).

The above experimental results were found to obey the following relation:

$$D = p_K - p_H - A\sqrt{m_{app.}}$$

where D, p_H and m_{app} have their usual significance and p_K is a constant. The constant A is the Debye-Hückel limiting slope of the activity coefficient. This relation is similar to that found by Walpole for the determination of the dissociation constant of acetic acid colorimetrically (*J. Chem. Soc.*, 1914, **105**, 2501; cf. Glasstone, "Intoduction to Electrochemistry", Van Nostrand, 1949, p. 324). The validity of this equation can be readily seen from the data in Table II.

TABLE II

D.	p_H.	$(m_{app})^{\frac{1}{2}}$.	pK.
0.468	1.33	0.239	1.68
0.452	1.35	0.231	1.69
0.420	1.40	0.214	1.71
0.396	1.46	0.202	1.75
0.388	1.48	0.198	1.77
0.366	1.53	0.187	1.80
0.341	1.60	0.173	1.85
0.322	1.66	0.162	1.90
0.302	1.71	0.152	1.94
0.253	1.85	0.128	1.94
0.212	1.98	0.108	2.03
0.202	2.00	0.102	1.69

The variation in the pK values arises from the assumption that the measured p_H's in glucose-water system represent true values; such an assumption is inadequate in Bates' sense (*Chem. Rev.*, 1948, **42**, 1). In spite of this approximation the mean value of 1.81 varies slightly over the whole range of the concentrations studied, and could be regarded as a measure of the tendency of glucose to behave as an acid under the influence of the electrostatic field of the proton.

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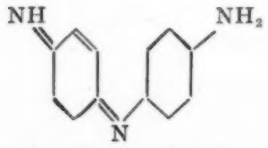
DYESTUFFS OBTAINED BY LINEAR CONDENSATION. PART I. POLYMERISATION OF *p*-CHLOROANILINE AND ALLIED COMPOUNDS

By Rajindar Kumar Kochar and Sikhibhushan Dutt

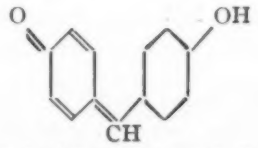
p-Chloroaniline and allied compounds have been polymerised to give rise to brown to blue dyes. Ordinarily, a halogen atom present in the nucleus of benzene is not active enough to undergo substitution reactions. Activity of a number of catalytic agents in this special application of the Ullmann reaction has been studied. The dye molecule appears to be highly complicated, perhaps it is akin to some of the compounds of the 'Aniline Black' series. The dyes, though basic in character, are highly substantive to Nylon fibre.

Dutt (*J. Chem. Soc.*, 1926, 1171) has shown that a dye molecule containing several chromophores of the same kind has almost the same absorption maxima as the dye containing only one such chromophore. While dyes containing two different and distantly situated chromophores have absorption maxima that are approximately intermediate in position to the maxima of the two components of the dye, each containing one chromophore. Hence, in each of the two above mentioned cases, the effects of the strains situated in distant positions in the molecule are independent of each other. But the effect produced, when two sources of strain are in close proximity in a molecule, is much greater than when they are remote from each other, because in the former case the intervening single linkage assumes a comparatively strained condition thereby increasing the total rigidity of the molecule. It is for this reason that the conjugated double bonds, that is alternate single and double linkages, have cumulative effect and are productive of intense colour, particularly when they are of considerable lengths, as has been shown by Sircar (*ibid.*, 1916, **109**, 757) in the azo series of dyestuffs. The absorption and the consequent production of colour becomes considerably intensified if nitrogen atoms are interspersed in the conjugate chain.

This is clearly seen in the colour and absorption maxima of the following compounds:



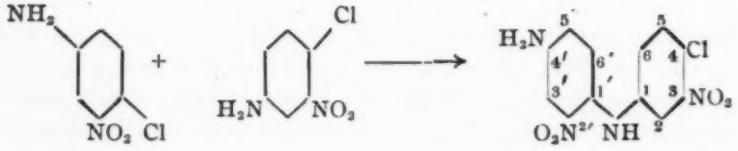
[Indamine, λ 6650 (blue)]



[*p*-Quinoyl-*p*-cresol, λ 4250 (yellow)]

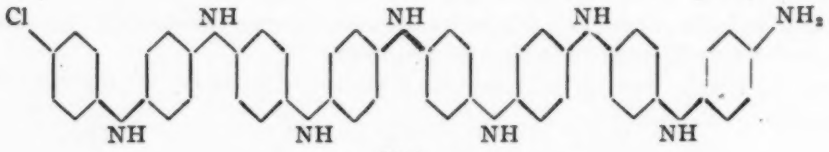
In the present paper, long conjugate chains of alternate single and double bonds containing interspersed nitrogen atoms have been built up by polymerisation or intermolecular condensation of *p*-chloroaniline and allied compounds and subsequent oxidation of the chian-polymers thus formed. The resultant products have been found to possess intense colour and good dyeing property, particularly for synthetic fibres, like Nylon, with long chain-polymer molecules.

When *p*-halogenated anilines are heated in presence of suitable catalysts, brown to blue-black substances are produced that have low solubilities in mineral acids but are fairly soluble in acetic acid. These dyes are substantive to Nylon and impart medium to heavy shades having a high degree of wet-fastness. Elementary analysis shows the presence in them of nitrogen and halogen, the type of halogen depending on the nature of the same in the starting material. Determinations of the molecular weight by Rast's camphor or diphenylamine methods show that a dye molecule containing eight or more benzene or benzene and diphenyl nuclei has been formed, which is also confirmed by the percentages of nitrogen and halogen in these compounds. Ordinarily a halogen atom attached to an aromatic nucleus is not active enough to undergo this type of reaction unless a nitro group is present in *ortho* or *para* position to activate it. For example, 3-nitro-4-chloroaniline (I) on heating is easily converted into 3:2′-dinitro-4-chloro-4′-amino-diphenylamine (II).



(I) (II)

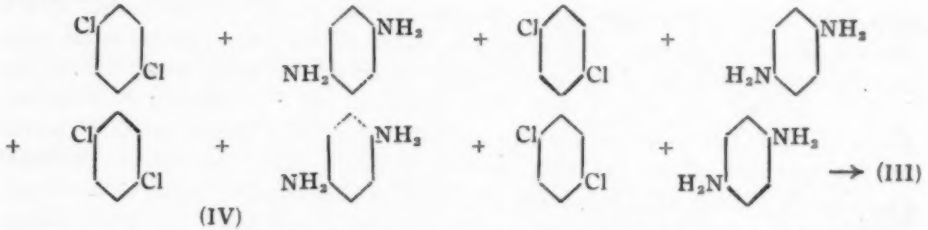
In the presence of copper powder, however, such a reaction takes place with great facility, as has been shown by Ullmann (*Ber.*, 1903, **36**, 2383; 1904, **37**, 853; 1905, **38**, 729). When *p*-chloroaniline is heated with copper for a long time (12 to 20 hours) at 200°, the above type of reaction does take place, but it proceeds much further than what has been shown above, with the result that eight molecules of the substance take part in the reaction with the formation of a linear condensation product (III), shown below, with the elimination of seven molecules of hydrogen chloride.



(III)

If the amino group in *p*-chloroaniline is protected, e.g. in *p*-chloroacetanilide, no reaction takes place even on prolonged heating and the unchanged product can be recovered in the end. 3-Nitro-4-chloroaniline, on the other hand, on heating with copper powder undergoes a similar type of linear condensation with the formation of a similar dyestuff. But if the nitro group is in the *meta*-position with respect to the halogen atom, e.g. 2-nitro-4-chloroaniline, then the reaction does not take place. *o*-Chloroaniline when heated with copper undergoes a reaction similar to *p*-isomer, but the yield of the final dyestuff is very poor. *m*-Chloroaniline does not undergo the condensation under any circumstances.

A modification of the above linear condensation of *p*-chloroaniline with the formation of a dyestuff can also be made by heating equivalent quantities of *p*-dichlorobenzene and *p*-phenylenediamine, when four molecules of the former condense with four molecules of the latter by alternate molecular linkages (IV) with the formation of the same dyestuff:



(IV) → (III)

In a similar way *p*-dichlorobenzene can also be condensed with *o*-phenylenediamine, benzidine and *o*-dianisidine with the production of similar dyestuffs. Instead of *p*-dichlorobenzene, which is rather too volatile at the temperature of the reaction, *p*-chloroiodobenzene or *p*-bromoiodobenzene can be more advantageously employed, as they are more reactive and less volatile and therefore afford better yields of the condensation products.

Polymerisation of p-*Chloroaniline*

When *p*-chloroaniline is heated with copper powder and the final product purified, a compound is obtained which is akin to Emeraldine (Green and Woodhead, (*J. Chem. Soc.*, 1912, **101**, 1117) in physical and chemical properties. The analytical data give it a formula $C_{48}H_{37}N_8Cl$ with a molecular weight of 760.5 which is close to the value of 745, as determined by the method of Rast. This indicates that the molecular formula of the compound is the same as the empirical formula. That the molecule is linear is indicated by the ready intake of the dye by Nylon fibre and the high value of the wet-fastness, a linear molecule being capable of lying along the molecular chain of the synthetic fibre, thus exerting the residual valency forces to the fullest extent, for, a crookedness in the molecule is a hindrance to the entry of the dye in the fibre. Similarities in properties to Emeraldine and the mechanism of formation point to a structure similar to that of the latter compound. Under such circumstances the molecule consists of eight benzene nuclei joined together by $-NH-$ bonds in a straight chain as has already been shown above. But such a compound will only be a leuco compound and will be unlikely to exhibit any colour for want of strain *i.e.*, conjugated double bonds in the molecule. The coloured compounds obtained are therefore oxidation products of the above leuco base. From the theoretical point of view there are four such oxidation products capable of existence (cf. Green and Woodhead, *loc. cit.*):

A — *p*-chloro-leuco-emeraldine (benzenoid), colorless
B — *p*-chloro-proto-emeraldine (mono-quinonoid)
C — *p*-chloro-emeraldine (di-quinonoid)
D — *p*-chloro-nigraniline (tri-quinonoid)
E — *p*-chloro-pernigraniline (tetra-quinonoid).

According to Green and Woodhead, who isolated similar compounds during the oxidation of aniline to Aniline Black, compounds A, B and E are unstable and under suitable conditions are readily transformed into C and D. Hence, in actual practice from *p*-chloroaniline, we get a mixture containing mainly C and D along with only traces of B and E. A, being highly unstable in presence of air or oxygen even in the dry state, is not likely to be present in the reaction product at all. When treated with a mineral acid in the presence of air or oxygen, all the various compounds are transformed practically completely into C and are then easily dissolved by acetic acid. Hence, this is the compound that results after the purification and crystallisation of the reaction products. That this compound contains two pairs of reactive double bonds is proved by the reduction of the dye with titanous chloride in accordance with the method of Green and Woodhead, when it is found that 0.55% of hydrogen (neglecting air correction) is necessary to fully saturate the compound to a pale grey leuco base. As to the assignment of these double bonds to any particular part of the molecule, there is still a speculation, though the production of intense colour points out to conjugation in the molecule. Hence, in all probability the dye corresponds, in constitution, to that of Emeraldine, (C), and the unpurified stuff contains a mixture of oxidation and reduction products of Emeraldine to various stages.

Catatytic Agents

Several catalytic agents that are likely to be useful in the elimination of hydrogen halide and subsequent oxidation of the reaction product were tried. Various metallic chlorides like those of zinc, calcium, tin, aluminium and iron, and metallic oxides like lead peroxide, cupric oxide, ferric oxide and carbon were found to be of no avail. Finely divided metals like sodium, potassium, iron, zinc, silver and copper were then tried with varying degrees of success. In the long run it was found that freshly precipitated copper powder and activated copper-bronze (containing 90% of copper) gave the best yields (75 to 85%) of the reaction product. The reaction could be carried out by heating the reactants either dry or in nitrobenzene solution with equal facility.

The raw materials used in the preparation of these dyes are quite cheap and the process of manufacture, easy. Hence, they are likely to be of value in commerce, particularly in the dyeing of Nylon fabrics where high fastness of the shade comparable to that of the supermilling dyes on wool, is required. The only drawback is their low solubility in water. Further work is in progress with a view to removing this defect.

EXPERIMENTAL

Activated Copper Powder and Activated Copper-Bronze.—They were prepared according to the method described by Vogel ("Practical Organic Chemistry", Longmann, London, 1948).

Polymerisation of p-*Chloroaniline*: *Preparation of Leuco*-p-*chloro-emeraldine and* p-*Chloro-emeraldine.*—Finely powdered *p*-chloroaniline (100 g.) was thoroughly mixed with activated copper powder (5 g.) and the mixture transferred to an air-tight heating apparatus connceted to a supply of pure dry nitrogen on the inlet side and to weighed potash bulbs on the outlet side. The heating was done at 120° for the first hour and

then at 180°-200° for the next 12 hours, maintaining a constant slow stream of nitrogen (2 bubbles per second) through the apparatus. At this stage the formation of the leuco compound was complete, and the evolution of hydrogen chloride ceased which was indicated by no further increase in the weight of the potash buibs. The heating was discontinued, but the stream of nitrogen was maintained until the melt reached the room temperature and completely solidified.

The light grey solid could not be obtained in the pure state due to the rapidity with which it was oxidised in the air with the formation of a blue dyestuff. Lumps of the solid are pale grey inside when freshly broken surfaces are exposed to view, but they soon turn dark blue by oxidation in the air. It was therefore thought to be expedient to convert the leuco base directly into the dyestuff.

The impure leuco compound, mentioned above, was again melted at 200° and a slow stream of oxygen was passed through it for an hour. The light grey compound turned intense blue with a glistening surface which was quickly poured out into a mortar, allowed to cool and finely powdered. It was then repeatedly extracted with alcohol to remove the unchanged *p*-chloroaniline. After washing in ether and drying in the air-oven at 60°, the product weighed 57 g.

It was next warmed with 200 c.c. of 1% sulphuric acid at 40°-50° for ½ hour and then filtered. This procedure was repeated until no more copper was extracted by the acid and the residue on incineration was found to be free from ash and copper. The copper-free substance weighed 50.3 g.

The dark blue powder was lixiviated with successive amounts of 10 parts of 80% acetic acid in the cold until the last extract showed only a pale blue colour. Most of the substance went into solution and only a small amount of a blue-black powder remained undissolved. The navy-blue acetic acid solution was diluted with water to twice its volume and the dyestuff precipitated by the addition of dilute hydrochloric acid. The insoluble hydrochloride was filtered off and converted into the free base by trituration with liquor ammonia. This was filtered off, washed with water, redissolved in 80% acetic acid, reprecipitated by dilute hydrochloric acid and the free base regenerated by liquor ammonia. The dried substance was finally crystallised from pyridine in navy-blue glistening prisms with a golden green irridescence. The yield of the final product was 35.2 g. The substance on heating above 250° undergoes slight decomposition and has therefore no definite melting point. It is insoluble in ether, alcohol, chloroform, benzene and ethyl acetate, and is only slightly soluble in acetone with a bright blue colour. It is easily soluble in acetic acid giving a sapphire-blue solution from which water does not precipitate the dyestuff. It dissolves easily in nitrobenzene and pyridine to dark blue solutions from which the dye is precipitated by the addition of other miscible solvents such as ether, alcohol, chloroform, benzene etc., and also water in the case of pyridine. The diluted acetic acid solution of the dyestuff dyes Nylon in brilliant shades of blue. [Found: N, 14.62; Cl, 4.62; M.W. (by Rast's method in camphor), 735; (in diphenylamine), 748. $C_{48}H_{39}N_8Cl$ requires N, 14.78; Cl, 4.76 per cent. M.W.,762.5].

Second Method.—The dyestuff, described above, was also prepared by heating the mixture of *p*-chloroaniline (100 g.) and activated copper powder (5 g.) in 200 c.c. of

nitrobenzene. The apparatus employed was similar to the one described before, but it was provided with a short reflux condenser and also a mercury sealed mechanical stirrer. The temperature was maintained at 160°-170° for a period of 20 hours, at the end of which the reaction was complete and evolution of hydrogen chloride ceased. After cooling, the dark indigo-blue solution was filtered to remove the copper, and from the filtrate the nitrobenzene was driven off by passing a current of steam. The residual dark blue powder was then subjected to purification and crystallisation as described before. The yield of the final product was 26 g. In this case the nitrobenzene being itself an oxidising agent, there was no formation of the leuco-base and hence no need of passing the oxygen. The dyestuff obtained by using nitrobenzene as a solvent was identical in all respects with the dyestuff prepared by dry heating of the constituents.

Preparation of Analogous Emeraldines.—Besides the compounds mentioned above, a few other aromatic amino and halogen derivatives were also subjected to similar treatments with the production of analogous Emeraldines. Their modes of preparation and properties are recorded in Table I.

Reduction of p-*Chloro-emeraldine with Titanous Chloride.*—The dyestuff (1 g.) was completely dissolved in glacial acetic acid (100 c.c.) by continuous stirring at the ordinary temperature. The solution was then made up to 250 c.c. by the addition of water. This solution (25 c.c.) containing 0.1 g. of the dyestuff was treated with 25 c.c. of a normal solution of titanous chloride in a stoppered 100 c.c. flask filled with carbon dioxide. After frequent shaking and standing for half an hour, by which time the dye solution became colorless, the excess of titanous chloride remaining in the flask was back-titrated with normal ferric alum solution, using ammonium thiocyanate as an indicator. From the amount of the titanous chloride used up in the reduction of the dye, the percentage of hydrogen required to saturate the dye molecule was found, which was 0.526%. Hence the compound contains two pairs of double bonds. In a similar way other dyestuffs of this series were also treated with titanous chloride to determine the amount of unsaturation present in the molecule. The values obtained corresponded with the presence of two double bonds in the molecule.

Oxidation of the Emeraldine with Ammonium Persulphate.—Various dyestuffs (1g.), prepared above, were dissolved in 10 c.c. of concentrated sulphuric acid and the solution cooled to 0° in a freezing mixture bath. A saturated solution of ammonium persulphate in water was then added dropwise to the dye solution with vigorous stirring, keeping the temperature below 5°. The colour of the solution soon darkened and became black, the intensity of the coloration being so great as to render it practically opaque. Addition of water to the black acid solution precipitated the oxidised dyestuff in black flocks, which were collected, washed with water and dried in the steam-oven. The jet-black powder, thus obtained, could not, however, be crystallised or obtained pure for analysis.

Application of the Dyes to Nylon Fabric.—The dye (5 g.) was dissolved in 20 c.c. of 80% acetic acid by heating for 10 minutes. To this solution were then added 200 c.c. of cold water and the Nylon sample put in. The temperature of the bath was then raised to 80° and kept there for a period of 3 to 4 hours. The dyed sample was then taken out and washed successively with water, dilute sodium carbonate and soap and finally rinsed in an ample supply of water and dried in the shade.

Nylon is a wonderful synthetic fibre containing a long aliphatic molecular chain and both acidic and basic groups, so that it is capable of being dyed by both acid and basic dyes. But the shades obtained by such dyes with Nylon from an aqueous bath are generally very light, due firstly to the water repellent properties of the fibre, and secondly to the dearth of 'active' groups in the fibre. In the series of dyestuffs, mentioned in the present paper, the dye molecule is extraordinarily long which enables it to orient itself and lie along the length of the polyamide molecular chain of the Nylon fibre. As the molecule contains a long conjugate chain, it possesses a high contingent of residual valence forces which enable it to anchor itself to the linear structure of the fibre molecule. This along with their low solubility is also the cause of the greater wet-fastness of the dyes.

TABLE I

No.	Reactants.	Appearance of the pure dyestuff.	Colour in soln.	Shade of dyeing on Nylon.	M.W. (Rast).	%Nitrogen*.
1.	*p*-Chloroaniline	Dark blue glistening prisms	Intense blue	Deep blue	735	14.35 (14.78)
2.	*o*-Chloroaniline	Violet-black spangles	Blue black	Dark blue	762	13.78 (13.91)
3.	*p*-Phenylenediamine and *p*-bromoiodobenzene	Indigo-blue scales	Dark blue	Deep blue	790	13.57 (13.91)
4.	*p*-Phenylenediamine and *p*-chloroiodobenzene	Do	Do	Do	752	14.64 (14.73)
5.	*o*-Phenylenediamine-2HCl and *p*-dichlorobenzene	Violet-black leaflets	Dark crimson	Dark crimson	737	14.48 (14.73)
6.	*o*-Phenylenediamine-2HCl and *p*-chloroiodobenzene	Do	Do	Do	742	14.77 (14.73)
7.	Benzidine and *p*-bromoiodobenzene	Deep violet-black scales	Violet-black	Dark violet	1090	10.15 (10.09)
8.	Benzidine and *p*-chloroiodobenzene	Do	Do	Do	1035	10.32 (10.52)
9.	*o*-Dianisidine and *p*-dichlorobenzene	Blue black spangles	Dark indigo-blue	Dark blue	1197	9.30 (9.45)
10.	*o*-Dianisidine and *p*-bromoiodobenzene	Do	Do	Do	1205	9.30 (9.11)
11	*o*-Dianisidine and *o*-dichlorobenzene	Dark violet tablets	Deep violet	Violet	1147	9.53 (9.45)
12.	*o*-Dianisidine and *p*-chloroiodobenzene	Blue black scales	Dark indigo-blue	Dark blue	1170	9.36 (9.45)

*Calculated values in parenthesis.

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THE DECOMPOSITION OF NITRIC OXIDE IN THE SILENT ELECTRIC DISCHARGE. PART II

By K. S. Visvanathan

The influence of the initial pressure of the gas on the rate of decomposition has been studied by exposing different amounts of the gas to a fixed applied potential for a fixed time. The dependence of the reaction rate on the applied potential has been investigated by subjecting a constant mass of gas to different applied potentials in the range 5-8.5 kV for a fixed time. The reaction rate is directly proportional to the applied potential for the range studied and decreases as the initial pressure increases. The applicability of the equation of Elliott Joshi and Lunt (*Trans. Faraday Soc.*, 1927, **23**, 57) for the velocity of chemical reactions in the silent electric discharge to the case of nitric oxide has been critically examined and its limitations discussed.

That the collision frequency of the reactant molecules is the primary determinant of the relevant thermal reaction does not hold for discharge reactions and that electrical factors affect the reaction rate greatly has long been recognised. Warburg (*Jahrb. Radioakt. Elektronik*, 1909, **6**, 181) from the formation and equilibrium of ozone, the decomposition of NH_3 etc. concluded that the effect might be photochemical. Brewer and Westhaver (*J. Phys. Chem.*, 1929, **33**, 883; 1930, **34**, 153, 1280, 2343) have enunciated what they call 'the law of photochemical equivalence' as a result of their synthesis of NH_3 in the glow discharge. They put forward a general equation for the rate of reaction viz., $dP/dt = \alpha I$, where dP/dt is the rate of reaction, I, the current and α, a constant independent of pressure and potential gradient. They attribute the chemical effect to positive ions.

Elliott, Joshi and Lunt (*Trans. Faraday Soc.*, 1927, **23**, 57) proposed a theory based on the concept of 'critical activation', the reacting molecule deriving its energy of activation from collisions with the ions (electrons) possessing or exceeding a certain minimum amount of energy. Thus, they deduce that chemical reactions in electrical discharge are to be related to excited rather than to ionised molecules. They derive the expression,

$$\frac{K}{p} = \frac{k}{e} i\epsilon^{-pkV_i/E_2}$$

where K denotes the number of molecules decomposing in one second in 1 c.c., p, the initial pressure of the gas in cm. Hg ; i, the conduction current through the ozoniser per sq. cm. in e.m. units, the electronic charge in e.m. units; V_i, the critical energy in volts of the colliding ion, related to the initial stage in the decomposition of the gas; E_2, the potential gradient across the annular space, and k, a constant given by $l = 1/p_K$, where l is the mean free path of the ion at the pressure p.

Experimental

The following series of experiments was conducted in order to ascertain the dependence of the reaction rate on the initial pressure of the gas, by determining the extent of decomposition by analysis of the system after a very short exposure. Nitric oxide was

taken in the ozoniser at initial pressures in the range 2—43.5 cm. and exposed to a constant applied potential of 5kV (r.m.s.) for a constant period of two minutes at the end of which time the gases were analysed in the usual way. The corresponding current, both at the beginning and at the end of an exposure was noted. The data are recorded in Table IA and represented graphically in Fig. 1. A similar series of experiments was conducted at an applied potential of 2.1 kV, the time of exposure remaining the same, viz., two minutes. The data are summarised in Table IB.

TABLE I

Dependence of the degree of decomposition of NO *on the initial pressure* (Fig. 1).

Time of exposure = 2 minutes.

Initial pressure of NO (cm.).	Initial mass of NO (millimol.).	Amount of NO decomposed. (millimol.).	Vol.% of NO decomposed.	Vol.% of N_2 formed.	Vol.% of NO_2 formed.	Discharge current *I* (milliamps).
		A. Applied potential = 5kV (r.m.s.).				
2.0	0.157	0 157	100.0	50.0	Nil	...
5.1	0.404	0.228	56.6	19.3	25.2	0.745
7.9	0.619	0.342	55.3	15.5	26.6	0.720
11.1	0.870	0.385	44.2	12.7	21.1	0 715
14.0	1.097	0.466	42.5	11.4	20.8	0.675
19.5	1.559	0 474	30.4	11.3	12.9	0.600
26.4	2.111	0.566	26.8	10.0	11 3	0.565
29.9	2 367	0.566	23.9	8.8	10.0	0.545
36.2	2.856	0.631	22.1	7.8	9.6	0.470
43.5	3.454	0.645	18.7	7.4	7.7	0.390
		B. Applied potential = 2.1kV (r.m.s.)				
2.6	0.210	0.086	40.9	13.3	18.5	0.35
4.2	0.339	0 122	36.0	9 5	17 7	0.41
9.0	0.727	0.193	26.5	7.7	12.6	0.32
12.4	1.000	0.153	15.9	5.6	7.0	0.29
16.0	1.290	0.170	13.7	4.7	6.1	0.21
20.5	1.656	0.236	14.3	4.4	6.6	0.195
26.2	2.123	0.178	8.4	2.9	3.7	0 14

The influence of the applied potential on the rate of decomposition of NO was studied by exposing the gas at a constant initial pressure of 10 cm. to different potentials in the range 5-8.5 kV for a constant period of one minute. After noting the final pressure, the gas was analysed.

TABLE II

Influence of applied potential on the rate of decomposition of NO (Fig. 2).

Initial pressure of NO = 10 cm. Period of exposure = 1 minute.

Applied potential (kV).	Final pressure of gas.	Vol. % of NO decomposed.	Vol. % of N_2 formed.	Vol. % of NO_2 formed.
5.0	9.30 cm.	36.0	8.5	18.3
6.0	9.15	40.3	10.0	20.1
6.5	9 10	44.1	10.4	22.4
8.0	8.90	52.1	12.0	26.6
8.5	8 80	52.8	12.4	26.9

Discussion

The pressure-time curves (cf. Figs. 2 and 3 of Part I, this *Journal*, 1952, **29**, 307) show that the rate of decomposition of NO falls as the initial pressure is increased, the applied potential remaining constant. It is seen from Table I (A and B) that as the initial pressure of NO is increased, the percentage by volume of NO decomposed in a given time, viz., 2 minutes, decreases; but this decrease in the rate of decomposition is not so rapid as the increase in the gas pressure.

A survey of the general literature shows that four different regions of gas pressure, for a given applied potential, may be distinguished in regard to the dependence of the rate of decomposition of a gas on its initial pressure. Thus:

(*i*) There is the 'unimolecular' region (Hutchison and Hinshelwood, *Proc. Roy. Soc.*, 1928, **117**, 131) where the amount of decomposition is proportional to the initial pressure, *i. e.*, the percentage amount decomposed is independent of the initial pressure; here X/p, *i. e.*, the ratio of the field strength X to the pressure p of the gas, which is the essential criterion for the energy which the ions acquire between impacts in an electric field, is high.

(*ii*) In this region the absolute amount decomposed in a given time increases; but the percentage change, however, decreases with increase in the initial gas pressure; here X/p is less than in (*i*). This is found to be the case with NO in the pressure range now investigated (cf. Table IA).

(*iii*) In this region the absolute amount decomposed remains the same; but the percentage decomposed decreases with increased gas pressure (cf. Joshi's results for N_2O, *Trans. Faraday Soc.*, 1927, **23**, 110). Region (*iii*) is characterised by X/p less than in (*ii*). It is interesting to observe that when NO in the range 2-43.5 cm. is exposed to 5kV, the absolute amount of NO decomposed increases, though the percentage decomposed diminishes with increase of gas pressure ; this corresponds to region (*ii*). However, when NO in the same range of gas pressure is exposed to a less intense field, viz., 2.1kV, so that X/p decreases, the absolute amount of NO decomposed over the pressure range is seen to remain nearly constant, though the percentage decomposed diminishes (cf. Table IB); this is region (*iii*).

(*iv*) Region (*iv*) will correspond to high initial pressures and comparatively reduced X/p where both the absolute amount decomposed and the percentage of decomposition will fall off rapidly with increase of gas pressure. Hence, in region (*iii*) and more especially in (*iv*), the velocity of decomposition will decrease more than linearly with increase of gas pressure.

It is again seen from Fig. 1 that the shape of the NO_2 curve conforms to that of an intermediate product formed in a consecutive reaction, thus confirming the validity of the mechanism proposed in Part I for the decomposition of NO in the silent electric discharge. Since the nature of the reaction products is seen to be independent of initial psessure and applied potential, it may be taken that the results of analysis reported in Table I(A and B) represent the various stages of one and the same reaction, those obtained at smaller pressures indicating the later stages and those at higher pressures, the earlier stages of the reaction. Thus regarded, the shape of the NO_2 curve is accounted for.

Table II (cf. Fig. 2) summarises the results obtained for the influence of the applied potential on the degree of decomposition of NO taken at a constant initial pressure of 10.0 cm. and exposed to various applied potentials for one minute. It is found that when the applied potential is not varied over too wide a range (actually it was varied from 5 to 8.5 kV), the degree of decomposition of the gas is linearly proportional to the applied potential. This is clearly brought out by Table III where θ/V and $\frac{\delta P/\delta t}{V}$ are calculated, θ being the volume percentage of NO decomposed, V, the potential applied, and $\delta P/\delta t$, the fall of pressure in unit time.

FIG. 1.

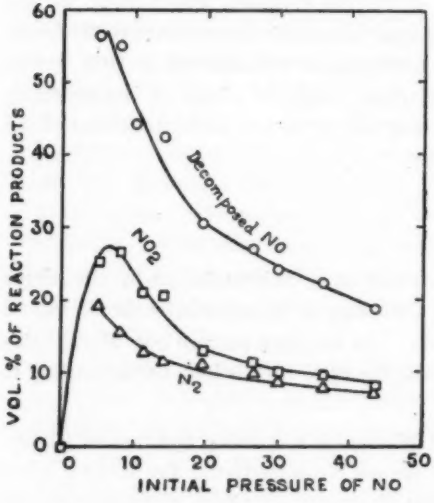

FIG. 2.

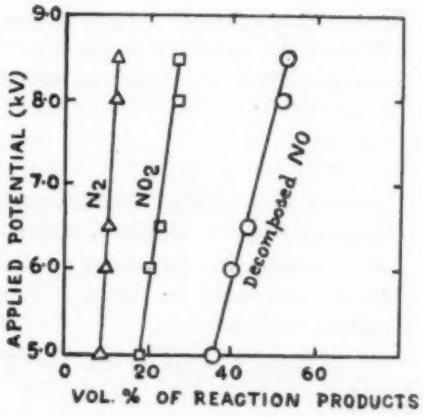

TABLE III

V (in kV).	θ_2	Fall of pressure in unit time (cm.)	θ/V.	$\frac{\delta P/\delta t}{V}$.
5.0	36.0	0 7	7.2	0.140
6.0	40.3	0.85	6 7	0.142
6.5	44.1	0.9	6.8	0.138
8.0	52.1	1.1	6.5	0.138
8.5	52.8	1.2	6.2	0 141

It is seen from the above table that both θ/V and $(\delta P/\delta t)/V$ are fairly constant.

According to Brewer and Westhaver (*loc. cit.*) the rate of a reaction in the glow discharge, as measured by the rate of change of pressure $\delta P/\delta t$, is proportional to I, the discharge current; *i.e.*, $\delta P/\delta t = \alpha I$, where I is independent of pressure. Now it is found from Tables II and III and from Fig. 2 that the degree of decomposition is linearly pro-

portional to the applied potential, *i.e.*, $\theta=\beta V$ and $\delta P/\delta t=\alpha V$ where α and β are constants. Since it is well known that at potentials at which ionisation by collision takes place in a gas, the current flowing through the gas increases exponentially with the applied potential, it is to be inferred from the relation: $\delta P/\delta t=\alpha V$ or $\theta=\beta V$ that $(\delta P/\delta t)/I$, (orθ/I) will not be constant but will decrease as I is increased. Thus, it appears that while Brewer and Westhaver's law holds good at the low pressures that they studied, viz., 0.1 to 4 mm., at the high pressures studied in the present investigation, the law is no longer valid. The degree of decomposition varies less than linearly with increase of current.

That θ, the percentage decomposition in a given time, should decrease as the initial gas pressure is increased or the applied potential is lowered, is deducible from the equation of Elliott, Joshi and Lunt (*loc.cit.*). Thus if v, N and t denote the volume of the annular space, the Avogadro constant and the time in seconds of exposure to discharge respectively, then Kvt gives the total number of molecules of NO changed in time t and pvN/RT, the number initially present. K/p therefore equals $A\theta$ where A is a constant. Also $i=I/S$, where I is the total r.m.s. current and S, the mean electrode area of the ozoniser. Hence, the equation may be written as

$$\theta = \frac{Bk}{e} I.^{-pkV_1/E_2}.$$

where B is a constant. The dependence of θ on p and on E_2 is brought out by the above equation. But it should be pointed out that according to the equation θ should fall off exponentially with increase of p or decrease of E_2. As has been pointed out above, this is true only when the pressures are very high and the ratio X/p is low, corresponding to regions (*iii*) and (*iv*).

It would thus appear that both Brewer and Westhaver's equation and that of Elliott, Joshi and Lunt hold good under restricted ranges of conditions, the former at low pressures and the latter at high pressures and that a general equation covering the behaviour of a gas under all conditions of pressure and applied potential is yet to be formulated.

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STUDIES ON (4-SUBSTITUTED 1:2-DIPHENYL)- 3:5-DIOXO-PYRAZOLIDINE DERIVATIVES

By S. L. Mukherjee, P. R. Gupta, S. L. Laskar and S. Raymahasay

Phenylbutazone, 4-*n*-butyl-3:5-dioxo-1:2-diphenylpyrazolidine, has been found to be an effective analgesic and antiarthritic compound. Certain other pyrazolidines have their uses in colour photography. Newer methods of syntheses to the known compounds and also of the unreported pyrazolidinediones have been described. The reducing properties of hydrazobenzene, similar to those of phenylhydrazine and hydrazine hydrate, have also been recorded.

Pyrazolone compounds are usually well known for their marked analgesic properties, and certain pyrazolidine derivatives are also found to have useful application in colour photography (Kendall *et al.*, U.S.P. 2427911/1947; B.P. 577260/1946). Lately, widespread interest has been created due to the introduction of 'phenylbutazone', 4-*n*-butyl-3:5-dioxo-1:2-diphenylpyrazolidine (Geigy, Swiss Pat. 266236/1951) in medicine as an effective analgesic and antiarthritic compound, superior to the other known compounds in the series. The present paper is the outcome of the authors' efforts to prepare a series of pyrazolidine-dione compounds for pharmacological evaluation. Preparation of certain 4-aryl-pyrazolidines, hitherto unreported, have been recorded along with the failure to produce 4-halogeno-substituted pyrazolidines, starting from halogeno-disubstituted malonic ester.

Pyrazolidine derivatives of this type are generally synthesised by the interaction of a suitably substituted or unsubstituted malonic ester with hydrazine hydrate, phenylhydrazine or hydrazobenzene in presence of sodium ethoxide (Ruhkoff, *Ber.*, 1940, **73B**, 820). It is postulated therein that the tendency of ring-formation decreases with the increase in size and unsaturation of the substituents in the malonic acid residue and hydrazines. More recently, a synthesis of this type of pyrazolidine-diones has been reported by the interaction of alkylmalonic esters with hydrazobenzene in presence of sodium ethoxide (Geigy, *loc. cit.*).

Prior to this, Tsumaki (*Bull. Chem. Soc. Japan*, 1931, **6**, 1) prepared 1:2-diphenyl-3:5-dioxo-pyrazolidine by reacting unsubstituted malonic acid dichloride with hydrazobenzene in ether. Other substitutions in the 1- and 2- position of the pyrazolidine nucleus included substituted aryl and heterocyclic rings (Kendall *et al.*, *loc. cit.*).

With a view to studying the reactivity of disubstituted malonic ester and disubstituted malonic acid dichloride with hydrazobenzene towards the formation of 4:4-disubstituted-1:2-diphenyl-3:5-dioxo-pyrazolidine, the reactions were tried under varying conditions. In the first case, with the employment of disubstituted malonic acid diethyl ester, no pyrazolidine-dione derivative could be isolated, whereas, when the condensation was tried between a disubstituted malonic acid dichloride of the type, alkyl-(or aryl-)halogeno-malonyl dichloride, as reported hereinafter, with hydrazobenzene in presence of ether and a tertiary base such as pyridine, diethyl- or dimethylaniline, we obtained only the de-halogenated 4-monosubstituted pyrazolidine-dione derivatives. This sort of remo-

val of halogen during the process has also been observed by Asher (*Ber.*, 1897, **30**, 1018) during the synthesis of 1-*p*-tolyl-3:5-dioxo-pyrazolidine through the reaction of chloro malonic ester with *p*-tolylhydrazine. He pointed out that the excess of tolylhydrazine was responsible for the removal of halogen from the chloromalonic ester. In our experiments, also, with halogen-substituted malonyl dichloride and hydrazobenzene, in molar proportions, it was observed that while some of the hydrazobenzene was used up in the formation of pyrazolidine nulceus, the remaining hydrazobenzene acted as the reducing agent. With the use of an excess of hydrazobenzene, however, no improvement on the yield could be achieved. The amount of the formation of azobenzene from hydrazobenzene corresponded to the pyrazolidine obtained. The reducing behaviour of hydrazobenzene was also observed when an alkyl-halogeno-malonic acid diester was made to react with hydrazobenzene in presence of ether and a tertiary base, in the way that hydrazobenzene was converted into azobenzene during the process and no pyrazolidine compound was obtained as the experimental conditions were not favourable towards cyclisation. Azobenzene, however, was obtained in a pure state from the reaction mixture. Such dehalogenation from the halogeno-malonic acid derivatives are long known in the literature to be exerted by hydrazine hydrate (Hirst and Macbeth, *J. Chem. Soc.*, 1922, **121**, 910, 2177) and monosubstituted arylhydrazines (Asher, *loc. cit.*).

This type of reducing properties in the removal of halogen was also observed by us when we prepared 4-bromo-substituted pyrazolidine compounds and treated them with hydrazobenzene, phenylhydrazine and hydrazine hydrate. In all the cases we obtained the dehalogenated compounds uniformly.

4-Aryl-substituted pyrazolidine-diones are hitherto unreported. The pharmacological investigations of the new pyrazolidine compounds are under progress.

Experimental

(*i*) *Ethylbromomalon Dichloride.*—Ethylmalonic acid (26.0 g.) was taken up in dry ether (75 c.c.) and bromine (32 g.), dissolved in dry ether, was added to it dropwise with mechanical stirring. The mixture was refluxed for ½ hour; ethereal solution was then washed with water, dried and evaporated and the residue was taken up in dry ether. The ether solution after drying was added dropwise to phosphorus pentachloride (85 g.) under cooling. After this reaction had subsided, the mixture was warmed on the water-bath for 1 hour. The ether and $POCl_3$ were removed and the residue was distilled under reduced pressure. Ethylbromomalon dichloride was obtained as a colorless liquid boiling at 78°-83°/10 mm.

(*ii*) iso*Propylbromomalon Dichloride.*—*iso*Propylmalonic acid (56 g.) was brominated in chloroform with bromine (64 g.). The bromo-*iso*propylmalonic acid was isolated as a crystalline solid, m.p. 120-22°. The bromo-acid was then treated with PCl_5 (100 g.) and the acid dichloride was collected at 95°-100°/18 mm.

(*iii*) n-*Butylbromomalon Dichloride.*— *n*-Butylmalonic acid (16 g.) was similarly brominated in ether with bromine (16 g.). The ether solution of bromo-*n*-butylmalonic acid was washed with water and dried over calcium chloride. The ethereal solution was

then added to PCl_5 in the cold, and the reaction was carried out as described above. *n*-Butylbromomalon dichloride was distilled and collected at 103°-108°/15 mm.

(*iv*) *Phenylbromomalon Dichloride.*—Phenylmalonic acid (9.0 g.) was brominated with bromine (9 g.) in ether. The ethereal solution of phenylbromomalonic acid was washed with water and dried over calcium chloride. This ether solution was next treated with PCl_5 (25 g.) as described under (*i*). Phenylbromomalon dichloride was distilled at 130°-135°/15 mm.

(*v*) p-*Chlorophenylmalon Dichloride.*—*p*-Chlorophenylmalonic acid (21 g.) was prepared from *p*-chlorobenzyl chloride by double carbonation through Grignard reaction in presence of an excess of *iso*propylmagnesium chloride (Ivanov and Spassov, *Bull. soc. chim.*, 1931, *iv*, **49**, 22). It was then dissolved in ether and treated with PCl_5 (42.0 g.). The acid dichloride was distilled and collected at 118°-120°/4 mm.

(*vi*) p-*Chlorophenylbromomalon Dichloride.*—*p*-Chlorophenylmalonic acid (21 g.) (prepared according to the method of Ivanov and Spassov, *loc. cit.*) was brominated with bromine (18 g.) in dry ether. The ethereal solution of *p*-chlorophenylbromomalonic acid was washed with water and dried over calcium chloride. This ether solution was next treated similarly with 42 g. of PCl_5 as described under (*i*). *p*-Chlorophenylbromomalon dichloride was collected at 135°-140°/6 mm.

(*vii*) 3:5-*Dioxo*-1:2-*diphenyl* 4-*ethylpyrazolidine.*—To a mixture of diethylaniline (15 c.c.), dry ether (150 c.c.) and bromoethylmalon dichloride (17.0 g.), held at 0°, was added hydrazobenzene (13 g.), dissolved in dry ether (50 c.c.) under stirring. After a few hours, the precipitated salt was filtered off and the ethereal solution was extracted with dilute alkali. The alkaline solution was next extracted with ether. The alkaline solution after treatment with charcoal was acidified with hydrochloric acid in the cold. 3:5-Dioxo-1:2-diphenyl-4-ethylpyrazolidine was thus precipitated and crystallised from alcohol, m.p.108°, yield 5.0 g. (Found: N, 9.6. $C_{17}H_{16}O_2N_2$ requires N, 10.0 per cent). (Mixed m.p. with an authentic sample, prepared according to Swiss Pat. 266239, was the same). The ether solution after extraction with dilute alkali was washed with cold dilute hydrochloric acid and water. The solid residue after removal of the ether was crystallised from alcohol and identified as azobenzene, m.p. 68-69°.

(*viii*) 3:5-*Dioxo*-1:2-*diphenyl*-4-*bromo*-4-*ethylpyrazolidine.*—3:5-Dioxo-1:2-diphenyl-4-ethylpyrazolidine (1.4 g.) was dissolved in chloroform (20 c.c.) and was brominated with bromine (1.0 g.), dissolved in chloroform (5 c.c.). The bromination was carried out at 60°-70° for ½ hour. The solvent was then removed and the residue crystallised from alcohol, m.p. 90-100°. (Found: N, 8.1. $C_{17}H_{15}O_2N_2$ Br requires N, 7.79 per cent).

(*ix*) *Debromination of* 3:5-*dioxo*-1:2-*diphenyl*-4-*bromo*-4-*ethylpyrazolidine.*—To a solution of 3:5-dioxo-1:2-diphenyl-4-bromo-4-ethylpyrazolidine (3.5 g.) in ether (50 c.c.) and pyridine (8 c.c.) was added hydrazobenzene (1.8 g.), dissolved in ether (50 c.c.) with stirring at 0°. After a few hours the precipitated solid was filtered off and the ethereal solution was extracted with dilute alkali. The alkaline solution was acidified with concentrated hydrochloric and the precipitated 3:5-dioxo-1:2-diphenyl-4-ethylpyrazolidine was crystallised from alcohol, m.p. 108°, yield 2.5 g. The mixed m.p. with an authentic sample was found to be the same. The ethereal solution after removal of pyrazolidine

compound and the basic solvent was evaporated and the residual solid was identified as azobenzene on crystallisation from alcohol, m.p. 68-70° (1.2 g.).

(*x*) 3:5-*Dioxo*-1:2-*diphenyl*-4-iso*propylpyrazolidine*.—A solution of hydrazobenzene (8.0 g.) in 10 c.c. of ether was added under stirring to a mixture of *iso*propylbromomalon dichloride (10.4 g.), ether (50 c.c.) and diethylaniline (20 c.c.), held at 0°. After the reaction, pyrazolidine compound was isolated as described under (*vii*), and crystallised from alcohol, m.p. 145°, yield 3.7 g. (Found: N, 9.36. $C_{18}H_{18}O_2N_2$ requires N, 9.52 per cent).

3:5-*Dioxo*-1:2-*diphenyl*-4-iso*propyl*-4-*bromopyrazolidine*.—3:5-Dioxo-1:2-diphenyl-4-*iso*propylpyrazolidine (5.8 g.), dissolved in chloroform, was brominated with bromine (3.5 g.). The bromopyrazolidine was crystallised from alcohol as white crystalline needles, m.p. 97-98°. (Found: N, 7.8. $C_{18}H_{17}O_2N_2$ Br requires N, 7.5 per cent).

3:5-Dioxo-1:2-diphenyl-4-*iso*propyl-4-bromopyrazolidine (3.7 g.) was similarly reduced to 3:5-dioxo-1:2-diphenyl-4 *iso*propylpyrazolidine (*x*) with hydrazobenzene (1.8 g.) in presence of ether and pyridine, m.p. 144-45° (alcohol).

(*xi*) 3:5-*Dioxo*-1:2-*diphenyl*-4-n-*butylpyrazolidine*.—A solution of hydrazobenzene (6.0 g.) in ether was added to a mixture of *n*-butylbromomalon dichloride (8.8 g.), ether and diethylaniline (15 c.c.). The reaction mixture was worked up as given under (*vii*) and the pyrazolidine compound was crystallised from alcohol as needles, m.p. 104-105°, yield 3.5 g. (Found: N, 9.2. $C_{19}H_{20}O_2N_2$ requires N, 9.09 per cent).

3:5-*Dioxo*-1:2-*diphenyl*-4-n-*butyl*-4-*bromopyrazolidine* was prepared from 3:5-dioxo-1:2-diphenyl-4-*n*-butylpyrazolidine (3.0 g.) and bromine (1.6 g.) in chloroform. The bromo compound was crystallised from alcohol, m.p. 116-18°, yield 3.2 g. (Found: N, 6.91. $C_{19}H_{19}O_2N_2Br$ requires N, 7.23 per cent).

3:5-Dioxo-1:2-diphenyl-4-*n*-butyl-4-bromopyrazolidine (3.8 g.) was similarly debrominated with hydrazobenzene (1.8 g.) in ether and pyridine, yield 2.6 g., m.p. 105°.

3:5-Dioxo-1:2-diphenyl-4-*n*-butyl-4-bromopyrazolidine (3.8 g.) was debrominated with phenylhydrazine (1.1 g.) or hydrazine hydrate (75 %, 1.0 c.c.) in ether in presence of pyridine. The debrominated pyrazolidine compound was extracted from the ether solution with dilute alkali and precipitated with hydrochloric acid. This was then crystallised from alcohol, m.p. 104-105°.

(*xii*) 3:5-*Dioxo*-1:2-*diphenyl*-4-*phenylpyrazolidine*.—Hydrazobenzene (22 g.), dissolved in ether (100 c.c.), was added to a mixture of phenylmalon dichloride (25 g.) and diethylaniline (25 c.c.) in ether (100 c.c.), held at 0°, with stirring. The precipitated material was filtered and taken up in alcohol and dilute alkali solution, charcolised and acidified with hydrochloric acid. The solid, thus obtained, was crystallised from alcohol as colorless needles, m.p. 184-85°, yield 12 g. (Found: N, 8.6. $C_{21}H_{16}O_2N_2$ requires N, 8.53 per cent).

3:5-*Dioxo*-1:2:4-*triphenylpyrazolidine* was also prepared from phenylbromomalon dichloride (8.7 g.) and hydrazobenzene (6 g.) in ether and diethylaniline (15 c.c.). The insoluble solid was filtered and treated as described above, m.p. 184°.

3:5-*Dioxo*-1:2:4-*triphenyl*-4-*bromopyrazolidine* was prepared from 3:5-dioxo-1:2:4-triphenylpyrazolidine (3.2 g.) and bromine (1.6 g.) in ether with stirring at 60°-80°.

The ether was then removed and the solid was crystallised from alcohol as pale yellow shining flakes, m.p. 160°, yield 3.5 g. (Found: N, 7.0. $C_{21}H_{15}O_2N_2Br$ requires N, 6.87 per cent).

3:5-Dioxo-1 : 2 : 4-triphenyl-4-bromopyrazolidine (4.0 g.) was debrominated to 3:5-dioxo-1 : 2 : 4-triphenylpyrazolidine with hydrazobenzene (1.8 g.) in ether in presence of diethylaniline, m.p. 184°.

(*xiii*) 3:5-*Dioxo*-1:2-*diphenyl*-4-*chlorophenylpyrazolidine*.—A solution of hydrazobenzene (11 g.) in ether was added to a mixture of *p*-chlorophenylmalon dichloride (15.0 g.) and diethylaniline (20 c.c.) in ether, held at 0°, with stirring. The insoluble residue was filtered and dissolved in alcohol containing dilute caustic soda solution. This solution was then charcolised, acidified with hydrochloric acid; pyrazolidine was filtered off and crystallised from alcohol a^S stout rod, m.p. 196-97°, yield 10.5 g. (Found: N, 8.0 $C_{21}H_{15}O_2N_2Cl$ requires N, 7.72 per cent).

3:5-Dioxo-1:2-diphenyl-4-*p*-chlorophenylpyrazolidine was also prepared by reacting *p*-chlorophenylbromomalon dichloride (13 g.) with hydrazobenzene (8 g.) in presence of ether and diethylaniline (25 c.c.), m.p. 196°.

The 4-bromopyrazolidine derivative of the above was prepared from the preceding compound (3.6 g.) and bromine (1.6 g.) in ether at 70°-80°. After removal of the solvent, the solid was crystallised from alcohol as pale yellow flakes, m.p. 119-20°, yield 3.0 g. (Found: N, 6.6. $C_{21}H_{14}O_2N_2ClBr$ requires N, 6.34 per cent).

The bromopyrazolidine (4.4 g.) was debrominated to 3:5-dioxo-1:2-diphenyl-4-*p*-chlorophenylpyrazolidine with hydrazobenzene (1.8 g.) in ether in presence of diethylaniline, m.p. 196°.

This work is under Patent application.

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DETERMINATION OF CUPROUS AND CUPRIC IONS FROM A SOLUTION OF THEIR MIXTURE: APPLICATION OF CITRATE COMPLEX FORMATION

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It has been observed that cuprous ions can be quantitatively oxidised with iodine in presence of a sufficient excess of sodium citrate. Based on this, a process has been developed for quantitative iodimetric estimation of cuprous and cupric ions from a solution containing their mixture. The cuprous copper is first determined in presence of an excess of citrate which forms a stable complex with cupric ions present originally as well as those formed during oxidation of cuprous ions. After this the citrate complex is decomposed with hydrochloric acid, and total copper determined in the usual manner. The cupric copper is calculated from the difference. The optimum amounts of sodium citrate and hydrochloric acid required have also been worked out.

Under optimum conditions, it is possible to determine both cupric and cuprous copper within an error of ± 1.0%. The maximum limits of cuprous and total copper for single titrations have been set at 0.125 g. and 0.150 g. respectively.

Cuprous chloride has often been used as a catalyst for various organic reactions, viz., condensation of acetylene with arseneous chloride (Hewett *et al.*, *J. Soc. Chem. Ind.*, 1949, **68**, 263T), hydrolysis of allyl chloride (Hatch and Estes, *J. Amer. Chem. Soc.*, 1945, **67**, 1730) etc. Pure samples of solid cuprous chloride have a pronounced tendency of being oxidised to basic cupric salt. It is thus sometimes necessary to estimate the purity of such samples, *i. e.* to determine cuprous and cupric ions from a solution containing both of them. In a recent study (*J. Ind. Chem. Soc., Ind. & News Ed.*, 1951, **14**, 90) of the chlorination of cuprous sulphide, the authors were required to determine the proportions of cuprous and cupric chlorides in the product. An approximate value was then given from a determination of the total copper and chloride content, as no satisfactory method was available for a more direct determination of these ions together.

Stepanayan (*Chem. Abst.*, 1937, **31**, 6133) proposed a method for the titration of a mixture of cuprous and cupric chloride together with free hydrochloric acid with the help of a standard potassium ferrocyanide solution using ammonium molybdate, and ammonium molybdate with ferric chloride as external indicators. Hatch and Estes (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 136) determined cupric chloride by first oxidising it with ferric alum, and determining the ferrous ion formed according to standard procedures. We did not find Stepanayan's method sufficiently accurate and reproducible, probably due to the use of an external indicator. On the other hand, that due to Hatch and Estes is handicapped by the fact that a separate determination of total copper has to be made before the cuprous/cupric ratio can be ascertained. In the present paper, a method of determination of both cuprous and cupric ions in a single solution is being proposed, through the use of a citrate complex.

In presence of a suitable excess of sodium citrate, cupric ions form a stable complex which, however, can be quantitatively decomposed with mineral acid. This information has been used by Hume and Kolthoff (*ibid.*, 1944, **16**, 103) for the determination of cupric copper in presence of oxidising agents such as potassium iodate, bromate etc. It has been observed by us that if to a solution containing both cuprous and cupric ions a sufficient excess of sodium citrate is added, the cupric ions form a stable complex. The cuprous ions can now be estimated with standard iodine solution, the quantitative progress of the reaction,

$$2\,Cu^{+} + I_2 \longrightarrow 2\,Cu^{++} + 2\,I',$$

being achieved due to the instantaneous *masking* of the cupric ions as they are formed, by the excess of sodium citrate present. After the cuprous determination is over, the cupric complex is decomposed with suitable amounts of mineral acid, and the total copper determined in the usual way. Thus, it has been possible to estimate both cuprous and cupric ions in the same solution. The investigation further includes the effects of the different variables, such as the amounts of sodium citrate and mineral acid on the titration.

Experimental

The chemicals employed in the investigation were all B. D. H. Analar quality (or Merck's guaranteed) reagents.

The cuprous chloride solution was prepared by dissolving the requisite quantities of the reagent in a 10% solution of $CaCl_2,2H_2O$ and preserved in an atmosphere of hydrogen employing arrangements commonly used for oxygen-sensitive solutions. Ammonium chloride can also be used in place of the calcium chloride (the solubility of cuprous chloride is greater in calcium chloride than in sodium or potassium chloride, and even hydrochloric acid).

Procedure.—A known excess of standard iodine solution was taken in a 250 c.c. conical flask together with sufficient sodium citrate solution (2-3 c.c. of 1*M* sodium citrate solution for each mg. atom o total copper present). A known quantity of cuprous chloride solution was added to it and the final volume made to nearly 100 c.c. with distilled water. The cuprous chloride quantitatively reacted with the iodine, the excess of which was determined with a standard sodium thiosulphate solution, using starch as an indicator. Starch was added towards the very close of the end-point, when the solution turned from green towards blue. The end-point was intense clear blue, and could be easily detected. After the titration was over, a quantity of 6*N*-HCl was added when the cupric complex was quantitatively decomposed, helped by the addition of a further quantity of potassium iodide. The liberated iodine was titrated with sodium thiosulphate in the usual manner. This gave the amount of total copper. An amount of potassium sulphocyanide should better be added towards the last end-point to facilitate complete decomposition of the citrate complex. A clear white permanent end-point was obtained.

Influence of the Amounts of Sodium Citrate

Cupric ions form an intense blue complex with citrates. The intensity has been observed by Ferrari (*Ann. Chim. Appl.*, 1948, **38**, 84) to reach a maximum for a molar ratio of Cu : citrate as 1 : 2. This indicates that in order to form the complex (1 : 1) a much larger proportion of citrate must be present in the solution. In the present titration, the amount of citrate should be sufficient to help instantaneous masking of the cupric ions (as they are formed from the oxidation of cuprous ions by iodine). This can be ensured by the use of a large amount of citrate as practised by Hume and Kolthoff (*loc. cit.*), but it has the disadvantage that a correspondingly large proportion of mineral acid would be needed subsequently for the decomposition of the complex. Effect of the variation of the proportions of sodium citrate has been shown in Table I.

TABLE I

Influence of the varying proportions of sodium citrate on the determination of cuprous copper.

Cu taken (cuprous).	Vol. of 1*M* citrate added.	Molar ratio (Cu/Cit.).	Cu found (cuprous).	Diff.	Remarks.
0.06388 g.	1.0 c.c.	1 : 1	0.05517 g.	−8.71 mg.	Very unstable end-point
0.06388	1.5	1 : 1 5	0.06226	−1.62	Do
0.06388	2.0	1 : 2	0.06323	−0.65	Good end-point
0.06388	2.5	1 : 2.5	0.06323	−0.65	Do
0.06388	3.0	1 : 3	0.06353	−0.35	Do
0.06388	4.0	1 : 4	0.06323	−0.65	Do

A small portion (less than 1.5%) of the cuprous chloride used actually oxidised to the cupric state during handling and preparation of the solution. The aliquots presented in the above table represent 0.06516 g. of copper as weighed. In this solution, however, total copper and cupric copper were separately determined by the use of a volumetric method, and the difference has been taken in column (1) in Table I. It will be noticed that with insufficient proportions of citrate, a very unstable end-point is obtained and the results are low (the first indication of the end-point being taken into consideration). A molar ratio of 1: 2 is quite satisfactory for the titration. Further quantities do not improve the conditions in any way, and should better be avoided. A uniformly negative error is understood to be due to a further aerial oxidation during withdrawal and titration, which, however, can be avoided by carrying out the titration in an anaerobic atmosphere.

Influence of the Amounts of Hydrochloric Acid on the Determination of Total Copper

The optimum requirements of sodium citrate being ascertained, the effects of the amounts of hydrochloric acid on the decomposition of the citrate complex, and as such the determination of the total copper (after the determination of the cuprous copper in the same solution) were then studied, and the relevant data are shown in Table II.

TABLE II

Influence of the amounts of HCl *on the decomposition on the citrate complex.*

The aliquots in the different titrations contained 0.06388 g. Cu^{+} and 0.00128 g. Cu^{++}. Molar ratio of Cu: Cit = 1: 2.

Cu taken (total).	6*N*-HCl added.	Cu found (total).	Diff.	Remarks.
0.06516 g.	0.25 c.c.	0.06485 g.	−0.31 mg.	Somewhat reddish end-point
0.06516	1.00	0.06516	Nil	Stable end-point
0.06516	1.25	0.06546	+0 30	Do
0.06516	1.50	0.06485	−0 31	Do
0.06516	4.00	0.06485	−0.31	Do
0.06516	6.00	0.06452	−0.64	Unstable end-point

The proportions of mineral acid required for decomposition of the citrate complex would naturally depend on the amounts of citrate used earlier. In order to overcome the buffer system citric acid-citrate, the amount of hydrochloric acid needed would tend to be larger than what should be required from stoichiometric considerations alone. Our results confirm this. In absence of a sufficient excess of hydrochloric acid an unsatisfactory end-point is obtained. A very large excess of hydrochloric acid is to be avoided as the end-point becomes unstable. For 2 c.c. proportions of 1 *M* sodium citrate, 1 c.c. of 6 *N*-HCl is sufficient, but an excess of up to 4 c.c. can be used without any harmful effect. It has also been noticed that instead of adding much excess of HCl, a few grams (2-5 g.) of potassium sulphocyanide can be used in order to obtain a sharp and accurate end-point. Excess quantity of sulphocyanide should be avoided.

Application of the Citrate Complex formation Method to the Determination of Cu^{+} *and* Cu^{++} *from a Solution containing their Mixture*

The optimum conditions for the determination of cuprous and total copper being set, determinations were next carried out with solutions having different proportions of cuprous and cupric chlorides. In all the titrations, results of which are presented in Table III, the molar ratio of citrate added was 2:1 with regard to total copper. And, 0.5 c.c. of 6 *N*-HCl was used per c.c. of molar sodium citrate solution. Although these proportions were found optimum in the previous sets of experiments, it will be noted that a considerable excess of these amounts can safely be used without any difficulty. Smaller proportions are to be avoided. With unknown solutions, it is recommended that a sufficient excess of the reagents should be used and after first titration, the proportions are to be adjusted according to the recommended optimum.

Different proportions of cuprous and cupric copper were taken in different titrations within the range of 0.06 g. to 0.220 g. total copper. With the cuprous proportions relatively low (0.03 g.) results of cupric copper are always within ± 1.0% ; values of cuprous copper vary by over 1.0% (+ ve) when the total copper exceeds 0.180 g. in single titrations.

TABLE III

Determination of Cu^{+} *and* Cu^{++} *in the same solution by employing the citrate complex formation.*

Expt.	Cuprous copper			Cupric copper		
	Taken.	Found.	Diff.	Taken.	Found.	Diff.
1	0.03194 g.	0.03195 g.	+0.01 mg.	0.03129 g.	0.03127 g.	−0.02 mg.
2	0.03194	0.03163	−0.31	0.06258	0.06292	+0.34
3	0.03194	0.03226	+0.32	0.09387	0.09450	+0.63
4	0.03194	0.03226	+0.32	0.12516	0.12600	+0.84
5	0.03194	0.03258	+0.64	0.15645	0.15778	+1.33
6	0.03194	0.03289	+0.95	0.18774	0.18877	+1.03
7	0.03194	0.03195	+0.01	0.03129	0.03127	−0.02
8	0.06388	0.06324	−0.64	0.03129	0.03163	+0.34
9	0.09582	0.09604	+0.22	0.03129	0.03124	−0.05
10	0.12776	0.12740	−0.36	0.03129	0.03164	+0.35
11	0.15870	0.15560	−3.10	0.03129	0.03416	+2.87
12	0.19164	0.18790	−3.74	0.03129	0.03440	+3.11

When the cupric copper is relatively low, results are satisfactory up to a cuprous copper of 0.127 g. Above this, the values of cuprous copper are low, and those of cupric copper correspondingly high. This clearly reveals that under these conditions the reaction, $2Cu^{+} + I_2 \longrightarrow Cu^{++} + 2I^{-}$, does not proceed quantitatively to the right direction. To be on the safe side, therefore, it is recommended that an aliquot (under the condition of experiment) should contain *less than* 0.125 g. of cuprous copper, and *less than* 0.150 g. of total copper.

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STUDIES ON GUM JEOL (*LANNEA GRANDIS*, ENGLER). PART X. THE ALDOBIONIC ACID

By S. N. Mukherjee, S. C. Chakravarti and R. N. Rai Choudhury

Studies in the electrochemical properties of substances from gum jeol have been extended in this communication to the case of aldobionic acid which is its ultimate hydrolytic product. The observed properties have been compared with those of its immediate parent body, jeolic acid, and also of the gum itself. Such a comparison reveals that the aqueous solution of this acid is not colloidal in character and the acid probably remains molecularly dispersed.

After reporting the properties of jeolic acid in Parts VII to IX of this series of communications (this *Journal*, 1953, **30**, 198, 201, 647), the next subject of investigation has been the study of the properties of the immediate degradation product of the acid, viz., the aldobionic acid which serves as the acid kernel of the whole gum and which has been shown to be the galactose-galacturonic acid in the present case, as reported in Part III of this series (Mukherjee and Chakravarti, *ibid.*, 1948, **25**, 113).

Variations of hydrogen-ion activity and specific conductance of the aqueous solution of this aldobionic acid as well as its interaction with bases, acids, neutral salts and non-electrolytes have form the subject matter of the present communication on the same line as in the case of jeolic acid, the principal object being to examine how far it resembles or differs from its immediate parent body (jeolic acid).

Experimental

The aldobionic acid has been obtained in the pure state by the method described in Part III of this series (*loc. cit.*). An aqueous solution of this acid was prepared by dissolving a weighed quantity of the dry acid in equilibrium water having specific conductance of 1.3×10^{-6} mho. The solution was perfectly clear and did not present a turbid appearance as in the case of jeolic acid. Examined under the ultramicroscope it did not show any evidence of the existence of a Tyndall cone.

Bases used for interaction with this acid were NaOH, KOH, $Ba(OH)_2$, $Ca(OH)_2$, and the salts were the corresponding chlorides. The acid whose interaction with this acid was examined was hydrochloric acid, and the non-electrolytes were acetone, ethyl alcohol and methyl alcohol. These reagents were either of 'guaranteed reagent' or of 'pro analysi' quality.

Properties referred to here have been hydrogen-ion activity, equivalent weight, equivalent conductance, dissociation constant etc. The working temperature was $35° \pm 0.1°$. A hydrogen electrode was used for measurement of p_H and for potentiometric titrations. Same measurements were satisfactorily checked with a glass electrode.

Discussion

Effect of Concentration on Electrochemical Properties

Hydrogen-ion Activity and Equivalent Conductance.—Effect of the variation of concentration of the aqueous solution on the hydrogen-ion activity (a_H) and the equivalent conductance has been shown in Table I.

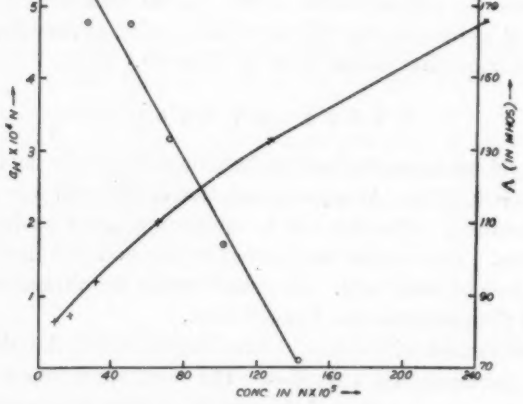
TABLE 1

Temp. = 35 ± 1°. Eq. wt. of the acid = 354. Sp. conductance of the water used = 1.3×10^{-6} mho.

Conc. (g./litre).	$N(=c)$.	$\sqrt{c}$.	p_H.	a_H.	Sp. cond. (mho) × 10^5. Obs.	Calc. from a_H.	Equiv. cond. (Λ).
0.03	8.47×10^{-5}	0.91×10^{-2}	4.23	$0.59 \times 10^{-4}N$	1.55	2.40	183.0 mho.
0.06	16.95	1.30	4.11	0.78	2.80	3.12	165.7
0.11	31.08	1.76	3.93	1.18	5.43	4.72	174.7
0.23	64.97	2.55	3.70	2.00	10.75	8.00	165.4
0.45	127.20	3.57	3.50	3.16	16.93	12.64	133.1
0.90	254.40	5 04	3.33	4.68	26.46	18.72	104.1
1.80	508.40	7 23	3 00	10.00	38 34	40 00	75.16

Variations of a_H against concentration in N and Λ against $\sqrt{c}$ have been shown in curves 1 and 2 respectively in Fig. 1. The a_H—concentration curve runs smooth as usual

FIG. 1



with slight concavity towards the concentration axis. $\Lambda - \sqrt{c}$ plot is roughly a straight line as envisaged by the Onsager relation $\Lambda c = \Lambda_0 - k\sqrt{c}$.

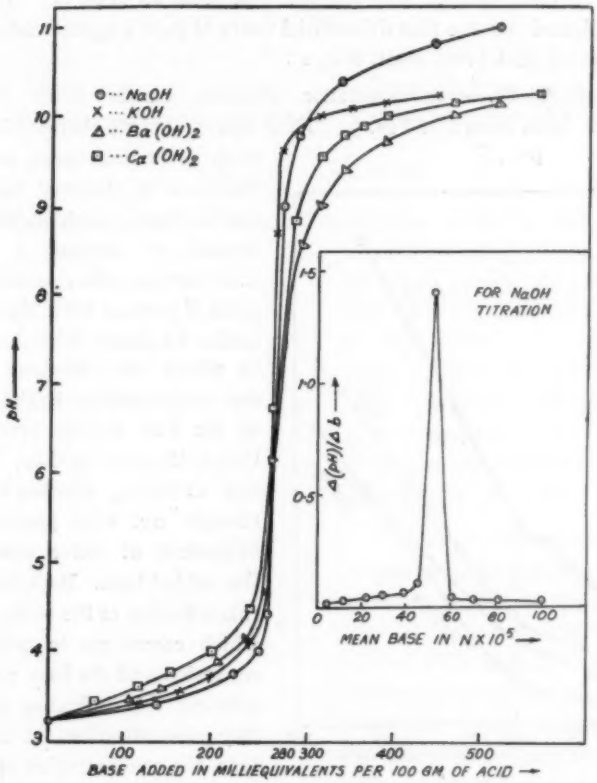
This feature of the $\Lambda - \sqrt{c}$ graph is commonly looked upon as characteristic of electrolytes in true solution and is unlike those observed in the case of jeolic acid or of the whole gum (vide Parts V and VII, this *Journal*, 1948, **25**, 339; 1953, **30**, 198). Thus, while the whole gum or jeolic acid shows some departure, the solution of the aldobionic acid in water may be regarded as a true solution like those of common electrolytes.

Another peculiar feature which will be observed from the above table is that the specific conductance values calculated from a_H (column 7) are lower than those observed (column 6)—a fact to be expected in the light of orthodox electrochemical considerations. In the case of jeolic acid (vide Part VII, *loc. cit.*) the observed values were higher, as also in the case of the whole gum (Part VI, *ibid.*, 1948, **25**, 531).

Interaction with Bases

Potentiometric Study.—The observations of potentiometric study (with 0.1% solution) have been graphically represented in Fig. 2. The general nature of the titration curves indicates the acid to be moderately strong and monobasic. The curves resemble those for hydrochloric acid closely.

FIG. 2



The p_H at the inflexion in all the cases is about 7.2 which is slightly towards the alkaline side. This indicates that the acid may be slightly weaker than acids like HCl. The total acidity amounts to 2.8×10^{-3} equivalents per g. of the acid or 280 m.e. (of base) per 100 g. of the acid. This agrees well with 270 m.e. obtained in conductometric titrations (*vide infra*).

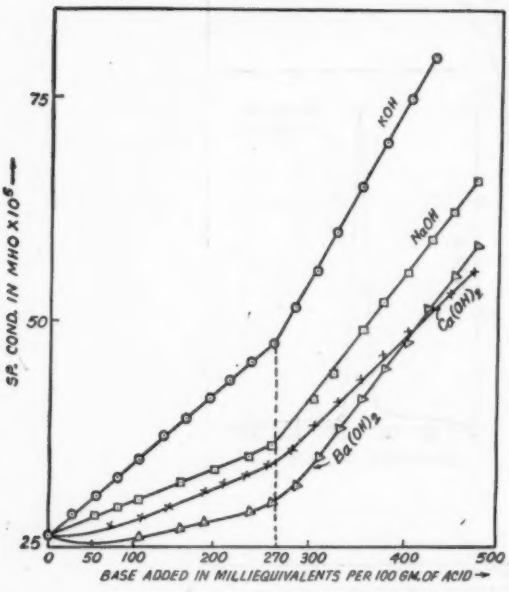
All the titration curves have initial flat portions which become shorter from NaOH to $Ca(OH)_2$ in the order: $NaOH > KOH > Ba(OH)_2 > Ca(OH)_2$. It is also interesting to note that final bends of the titration curves beyond inflexion occur earlier with $Ba(OH)_2$ and $Ca(OH)_2$ than with NaOH or KOH. Although the curves show some apparent divergence, they almost coincide at the inflexion point so that the total acidities are almost the same in every case.

This identity of total acidity with the different bases constitutes a very significant contrast to the behaviour of jeolic acid in its interaction with bases. The cationic effect appears to be almost absent, a fact which has been further corroborated by its interaction with neutral salts (*vide infra*). The acid thus resembles a true acid more than a colloidal acid where the total acidity has been found to be indefiuite quantity varying with the base.

The titration curves presented only one inflexion point up to p_H 11. This point has been further confirmed by the first differential curve ($\delta p_H/\delta b$ against mean base) which showed only one sharp peak (vide inset, Fig. 2).

Conductometric Study.—Conductometric titration curves (with 0.1% solution of the acid) have been shown in Fig. 3. They represent some characteristic features of weak acids in as much as specific conductance is observed to increase from the beginning with addition of the base instead of showing a diminution as with strong acids. Only one inflexion point is evident with NaOH and KOH unlike its parent substance, jeolic acid, in which two inflexions were observed, one corresponding to the neutralisation of the free acidity and the other to that of the total acidity. With $Ba(OH)_2$ and $Ca(OH)_2$, another inflexion point, though not very prominent, seems to be present at lower concentrations of the added base. Both these bases show this inflexion at the same concentration which comes up to about 5.1×10^{-4} equivalents of the base per litre. Considering this inflexion as that due to the neutralisation of free hydrogen ions, the concentration of free or active hydrogen ions amounts to 5.1×10^{-4} equivalents per litre of the solution (or per g. of the acid). This is expected to show a p_H of 3.27 for a solution of concentration 28.25×10^{-4} equiv./litre. The observed value is 3.20 which is an excellent agreement (cf. also data in column 4, Table I).

FIG. 3



The second inflexion point in each curve occurs at almost the same amounts of all the bases studied here, viz. at about 270 m.e. of the base per 100 g. of the acid. The equivalent weight therefore amounts to 370. Assuming the acid to be composed of one molecule of galactose and one of galacturonic acid, the calculated equivalent weight should be 354. The agreement between the calculated and observed value is thus fair.

The ratio of free to total acidity (a_H/C_H) amounts to $5.1 \times 10^{-4}/27 \times 10^{-4} = 0.19$ or 19%, which reveals the weak nature of the acid. This value is lower than that observed

for jeolic acid solution of the same concentration where it is about 25%. This is what is expected because the jeolic acid molecule contains a larger number of sugar molecules than the aldobionic acid, and hence, a 0.1% jeolic acid solution is more dilute with respect to the ionisable -COOH groups than the latter.

The dissociation constant of the acid as calculated from Ostwald's dilution formula

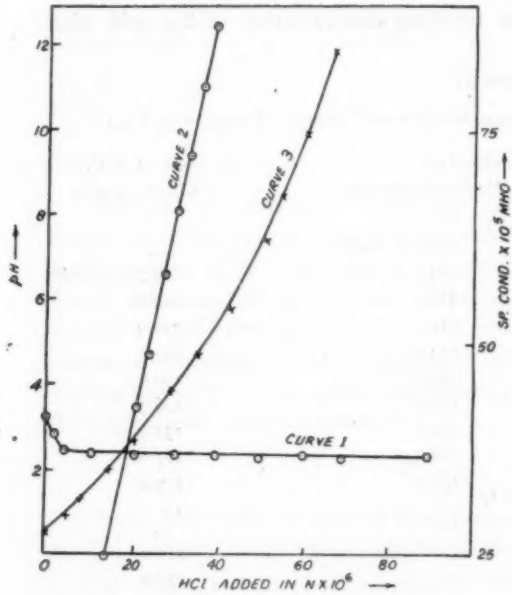
$$K = \frac{(a_H)^2}{C_H - a_H}$$

amounts to $K = 1.259 \times 10^{-4}$ with $a_H = 5.38 \times 10^{-4}$ and $C_H = 28.3 \times 10^{-4}$. The dissociation constant of the jeolic acid was 3.3×10^{-4} (vide Part VII of the series, *loc. cit.*). The aldobionic acid has thus roughly the same order of strength as the jeolic acid.

Interaction with Acids

Results of this study appear in Fig. 4. The addition of HCl to this acid (10 c.c. of a 0.1% solution) produces little change in p_H as shown in curve 1 (cf. the behaviour of the jeolic acid, Part VII of this series, *loc. cit.*). Thus, both jeolic acid and its aldobionic acid show some buffering towards acids which is in conformity with the buffering properties possessed by the gum itself (vide Part V, *loc. cit.*).

FIG. 4



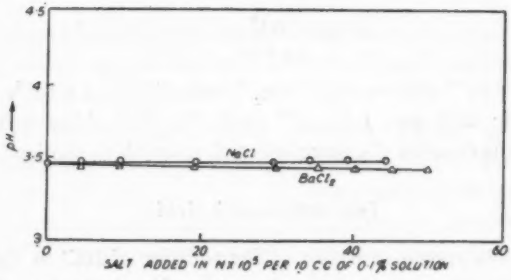
Specific conductances were also measured simultaneously with increasing addition of HCl to this acid (curve 2, Fig. 4). Specific conductance plotted against HCl added shows a steep and linear rise in the control experiment with water (curve 3), whereas the curve for the aldobionic acid is not so steep. This is roughly in conformity with the buffering properties mentioned above.

Interaction with Neutral Salts

Neutral salts were observed to be without any appreciable effect on the p_H of the solution even when added in considerable amounts. NaCl and $BaCl_2$ only were tried on a 0.1% solution and the results appear in Fig. 5. Curves run almost parallel to the concentration axis. These observations suggest that there is probably no liberation of hydrogen ions into the solution as with jeolic acid.

Measurements of specific conductance with increasing addition of NaCl and $BaCl_2$ have been shown in Table II. In this a definite volume of the acid solution was always mixed with an equal volume of the salt solutions having different concentrations such that the strength of the acid solution after mixing was reduced to half its original value.

FIG. 5



An acid solution of higher strength (1%) was used in this case to make the effects of interaction (if any) more prominent and the resulting concentration of the acid after mixing was 0.5%.

TABLE II

Sp. cond. of the aldobionic acid at 0.5% conc. $= 108 \times 10^{-5}$ mho. Temp. $= 35 \pm 0.1°$.

Conc. of salt.	Specific conductance observed of NaCl-H_2O mixture.	NaCl-acid mixture	Sp. cond. of NaCl-acid mixture (calc.)
	(*a*) NaCl.		
$0 \times 10^{-5}N$	0.13×10^{-5} mho	108×10^{-5} mho	...
3	5·7	114	113.7×10^{-5} mho
5	10.0	119	118.0
7·5	13.0	123	121.0
15.0	23·5	133·5	131.5
20.0	31.0	140.0	139.0
25.0	33·7	147.6	146.7
30.0	43·4	151.0	151.4
35.0	55.0	162.0	163.0
40.0	65.2	172.0	173.2
	(*b*) $BaCl_2$.		
0	0.13	108	...
2.5	10.0	116	118 0
5.0	20.0	125	128.0
12.5	44.0	150	152 0
20.0	55.0	161	163.0
25.0	81.0	185	189.0
30.0	90.0	195	198.0

It will be evident from the above table that the specific conductance observed by the addition of NaCl to the aldobionic acid is roughly equal to the sum of the specific conductances of the two at corresponding concentrations. Results of similar study in the case of gum itself have shown (vide Part VI, *loc. cit.*) that the observed specific conductance is slightly less than this additive value.

Interaction with Non-electrolytes

Three different protophilic non-electrolytes, viz., ethyl alcohol, methyl alcohol and acetone, were examined in this case. None of these appeared to precipitate this out of the aqueous solution in the concentrations studied herein. In fact, with methyl alcohol the acid was observed to be precipitated only when the alcohol was added to the aqueous solution to the extent of 700% by volume.

In these experiments, to a definite volume of the acid solution containing 1 g. of the acid per litre of the solution, was added an equal volume of non-electrolyte—water mixture in proper proportions to adjust the composition of the final mixture to the required percentage. The concentration of the acid in the final mixture was thus kept constant at 0.5 g. per litre. The zero concentrations of the non-electrolytes indicate that an equal volume of water only has been added in these cases.

Influence of these non-electrolytes on the hydrogen-ion activity of the acid solution is small as seen from Table III.

TABLE III

Conc. of non-electrolyte by vol.	Observed p_H with MeOH.	EtOH.	Acetone.
0 %	3.40	3.40	3.40
20	3.37	3.38	3.39
40	3.39	3.38	3.38
50	3.40	3.41	3.42

The p_H does not appear to change unlike that in the case of jeolic acid. The behaviour of this acid is thus, in some respects, different from those of the complex jeolic acid as well as of the whole gum from which it is derived by hydrolytic degradation. From the above it is obvious that although the dielectric constant of the solution is greatly altered by the addition of the non-electrolytes, the hydrogen-ion activity does not change appreciably. This is contrary to the expected behaviour according to orthodox electrochemistry. This point, however, requires further investigations before any definite conclusion can be arrived at.

CONCLUSION

From the results reported in this communication it is evident that the aldobionic acid of the gum Jeol (*Lannea grandis*, Engler)

(*i*) shows variations of hydrogen-ion activity and equivalent conductance with concentration and the square root of concentration respectively which can be compared to those of normal electrolytes (as distinguished from colloidal electrolytes showing aggregate formation);

(*ii*) shows potentiometric titration curves with strong monobasic acid with neutralisation at about p_H 7.2;

(*iii*) shows conductometric titration curves of weak acids with one inflexion point only; where there are two such inflexion points, the first one may be attributed to the neutralisation of free acidity and the second, to the total acidity;

(*iv*) possesses a definite total acidity uninfluenced by the nature of the base used for titration having its equivalent weight roughly 370, the degree of dissociation of 0.1% solution to be about 19% and the dissociation constant of the order of 10^{-4};

(*v*) possesses some buffering properties as revealed by its interaction with acids; in this respect it shows some similarity with the whole gum and the complex jeolic acid from which it is derived;

(*vi*) shows no base-exchange with neutral salts which yield an almost additive specific conductance with this acid proving thereby that neutral salts do not enter into any type of interaction;

(*vii*) shows no evidence of appreciable change in hydrogen-ion activity in presence of protophilic non-electrolytes as observed with jeolic acid.

The aldobionic acid is thus like an ordinary acid. The jeolic acid, its immediate parent body, shows some characteristics of colloidal electrolytes discussed in Part IX of this series (this *Journal*, 1953, **30**, 647).

The behaviour of the aldobionic acid can, however, be understood on the light of its origin. It is derived by the hydrolysis of the jeolic acid which forms a colloidal solution in water and is much smaller in dimension compared to the latter due to peeling off of some of the sugar molecules which are present in the parent acid. This diminution in size probably reduces it to molecular dimensions in aqueous solution and the properties (like base exchange, etc.) which are directly attributed to the larger surfaces prevailing in particles of colloidal demensions are thus absent in this case.

The authors' best thanks are due to Dr. H. L. Roy for his kind interest in this investigation.

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COMPOSITION OF URANYL FERRO- AND FERRICYANIDES BY PHYSICO-CHEMICAL METHODS. PART III. THERMOMETRIC STUDIES ON THE COMPOSITION OF URANYL FERROCYANIDE

By Jagdish Narain Gaur, H. C. Gaur and Abani K. Bhattacharya

The composition of uranyl ferrocyanide has been determined by thermometric titrations. The composition of the compound obtained by this method by adding uranyl nitrate to potassium ferrocyanide (direct method) corresponds to the type $K_2(UO_2)_3Fe(CN)_6.xUO_2(NO_3)_2$ and the same type of compound is also indicated by adding potassium ferrocyanide to uranyl nitrate (reverse method). The observations made by conductometric and potentiometric titrations are in agreement with the results of thermometry.

In continuation of the studies on the composition of uranyl ferrocyanide by conductometry and potentiometry, thermometric titrations have also been performed. It is interesting to observe that the composition of uranyl ferrocyanide indicated by conductometry and potentiometry is supported by the results of thermometric titrations. The three physico-chemical methods indicate the formation of adsorption complexes with uranyl nitrate. The results by thermometry are recorded herein.

Experimental

The thermometric titration arrangement was similar to that adopted by Dutoit (*J. chim. phys.*, 1921, **14**, 324). The reagents used were of 'Analar' (B. D. H.) quality. Potassium ferrocyanide solution was estimated as described in our previous publication (this *Journal*, 1951, **28**, 473). Uranium in uranyl nitrate solution was estimated as U_3O_8 by evaporating 25 c.c. of the prepared (A/2) solution, in a platinum crucible, on a water-bath and heating the residue in full flame of a Mecker burner until the weight of the precipitate was constant. Using different concentrations of the two salts in solutions, the titrations were followed by the direct and the reverse methods, *i.e.* when uranyl nitrate solution from burette was added to potassium ferrocyanide taken in Dewar's flask and *vice versa*. Titrations were also carried out in the presence of alcohol up to the total concentration of 20% by volume, after ascertaining by blank experiments that the rise in temperature on mixing water to the solution of $K_4Fe(CN)_6$ or $UO_2(NO_3)_2$ was negligible. The blank experiment was performed thus :

$K_4Fe(CN)_6$ or $UO_2(NO_3)_2$ solution containing 20% alcohol was left overnight and water was gradually added from the burette, 1 c.c. each time. The total rise in temperature with the addition of an equal volume of water was only 0.005°.

A/1-$UO_2(NO_3)_2$ solution corresponds to $M/5.1$.

A/1-$K_4Fe(CN)_6$ solution corresponds to $M/4.75$.

TABLE I

Direct titrations.

A/1-Uranyl nitrate and A/10-$K_4Fe(CN)_6$ (20 c.c.).

Alcohol = nil. (Fig. 1, curve 1).

A/1-Uranyl nitrate.	Temp.	Total rise in temp.	A/1-Uranyl nitrate.	Temp.	Total rise in temp.
0.0 c.c	2.950	0.00°	2.0 c.c	3.080	0.130
0.2	2.955	0.005	2.2	3.095	0.145
0.4	2.965	0.015	2.4	3.310	0.160
0.6	2.980	0.030	2.6	3.120	0.170
0.8	2.920	0.040	2.8	3.130	0.180
1.0	3.005	0.055	3 0	3.140	0.190
1.2	3.020	0.070	3.2	3.150	0.200
1 4	3.035	0.085	3.4	3 160	0.210
1.6	3.050	0.100	3.6	3.170	0.220
1.8	3.065	0.115	3.8	3.180	0.230

TABLE II

Reverse titrations.

A/2-Potassium ferrocyanide and A/10-uranyl nitrate (20 c.c.).

Alcohol = nil.

A/2 $K_4Fe(CN)_6$.	Temp.	Total rise in temp.	A/2-$K_4Fe(CN)_6$.	Temp.	Total rise in temp.
0.0 c.c.	2.980	0.000	2.2 c.c.	3.170	0.190
0.2	2.990	0.010	2.4	3.190	0.210
0.4	3.010	0.030	2.6	3.210	0 230
0.6	3.030	0.050	2.8	3.225	0.245
0.8	3.045	0.165	3.0	3.250	0.270
1.0	3.064	0.084	3.2	3.265	0.285
1.2	3.080	0 100	3.4	3.280	0.300
1.4	3.100	0.120	3.6	3.290	0.310
1.6	3.116	0.136	3.8	3.305	0.325
1.8	3.130	0.150	4.0	3.320	0 340
2.0	3.155	0.175	4.2	3.330	0 350

DISCUSSION

The results of the thermometric titrations are summarised in the following tables.

TABLE IIIA

Direct titrations.

A/10-$K_4Fe(CN)_6$ in the thermos flask (V c.c.).	Alcohol added.	$UO_2(NO_3)_2$ required for of A/10 $K_4Fe(CN)_6$ (V_1 c.c.).	$UO_2(NO_3)_2$ calc. for 20 c.c. of A/10 $K_4Fe(CN)_6$ ($V_1/V\times20$).	Equivalent vol. of A/10 $UO_2(NO_3)_2$ [$n(V_1/V)20$].	Compound
		A/1 and A/10.	Conc. ratio $n=10:1$.		
20	0	2.50	2.50	25.0	$K_2UO_2FeCy_6$, $0.16UO_2(NO_3)_2$
18	2	2.17	2.41	24 1	$K_2UO_2FeCy_6$, $0.12UO_2(NO_3)_2$
16	4	1.87	2.34	23.4	$K_2UO_2FeCy_6$, $0.094UO_2(NO_3)_2$
		A/2 and A/10.	Conc. ratio $n = 5:1$.		
20	0	4.96	4.96	24.8	$K_2UO_2FeCy_6$, $0.15UO_2(NO_3)_2$
18	2	4.32	4.80	24.0	$K_2UO_2FeCy_6$, $0.11UO_2(NO_3)_2$
16	4	4.77	4.72	23.6	$K_2UO_2FeCy_6$, $0.098UO_2(NO_3)_2$

TABLE IIIB

$M/5$-$K_4Fe(CN)_6$ in the thermos flask (V c.c.).	Alcohol added.	$UO_2(NO_3)_2$ required for V c.c. of $M/5$-$K_4Fe(CN)_6$ (V_1 c.c.).	$UO_2(NO_3)_2$ calc. for 20 c.c. of $M/5$-$K_4Fe(CN)_6$ ($V_1/V \times 20$).	Compound.
		$M/5$ and $M/5$. Conc. ratio n = 1 : 1.		
20	0	23.3	23.3	$K_2UO_2FeCy_6$, $0.16UO_2(NO_3)_2$
18	2	19.8	22.0	$K_2UO_2FeCy_6$, $0.10UO_2(NO_3)_2$
16	4	16.9	21.12	$K_2UO_2FeCy_6$, $0.056UO_2(NO_3)_2$
$M/2.5$		$M/2.5$ and $M/2.5$. Conc. ratio n = 1 : 1.		
20	0	24.0	24.0	$K_2UO_2FeCy_6$, $0.12UO_2(NO_3)_2$
18	2	20.1	22.3	$K_2UO_2FeCy_6$, $0.11UO_2(NO_3)_2$
16	4	16.6	20.75	$K_2UO_2FeCy_6$, $0.03UO_2(NO_3)_2$

TABLE IVA

Reverse titrations.

Theo. value : 20 c.c. of $UO_2(NO_3)_2$ ($M/5.1$) = 18.62 c.c. of $K_4Fe(CN)_6$ ($M/4.75$).

A/10-$UO_2(NO_3)_2$ in the thermos flask. (Vc.c.)	Alcohol added.	$K_4Fe(CN)_6$ required for V c.c. of A/10 $UO_2(NO_3)_2$ (V_1 c.c.).	$K_4Fe(CN)_6$ calc. for 20 c.c. of A/10 $UO_2(NO_3)_2$ [$(V_1/V)20$].	Equiv. vol. of A/10 $K_4Fe(CN)_6$ [$n(V_1/V)20$].	Compound.
		A/2 and A/10. Conc. ratio n = 5 : 1.			
20	0	3.20	3.20	16.0	$K_2UO_2FeCy_6$, $0.16UO_2(NO_3)_2$
18	2	3.02	3.36	16.8	$K_2UO_2FeCy_6$, $0.108UO_2(NO_3)_2$
16	4	2.72	3.40	17.0	$K_2UO_2FeCy_6$, $0.095UO_2(NO_3)_2$
		A/4 and A/10. Conc. ratio n = 2.5 : 1.			
20	0	6.52	6.52	16.3	$K_2UO_2FeCy_6$, $0.14UO_2(NO_3)_2$
18	2	5.97	6.64	16.6	$K_2UO_2FeCy_6$, $0.12UO_2(NO_3)_2$
16	4	5.45	6.81	17.02	$K_2UO_2FeCy_6$, $0.09UO_2(NO_3)_2$

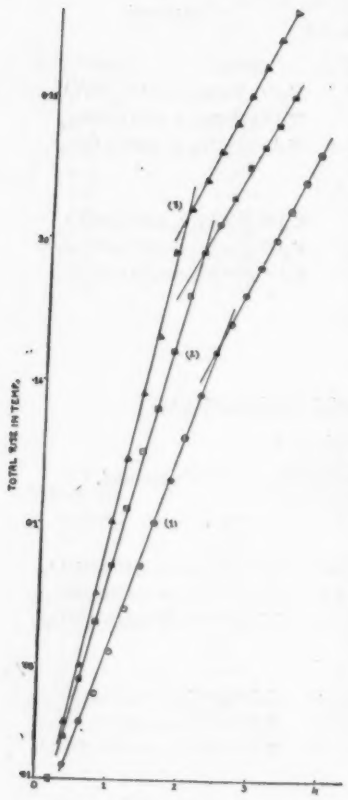
TABLE IVB

$M/5$-$UO_2(NO_3)_2$ in the thermos flask (V c.c.).	Alcohol added.	$K_4Fe(CN)_6$ required for V c.c. of $M/5$ $UO_2(NO_3)_2$ (V_1 c.c.)	$K_4Fe(CN)_6$ calc. for 20 c.c. of $M/5$ $UO_2(NO_3)_2$ ($V_1/V \times 20$).	Compound.
		$M/5$ and $M/5$. Conc. ratio n = 1 : 1.		
20	0	17.0	17.0	$K_2UO_2FeCy_6$, $0.17UO_2(NO_3)_2$
18	2	16.1	17.88	$K_2UO_2FeCy_6$, $0.11UO_2(NO_3)_2$
16	4	15.9	19.89	$K_2UO_2FeCy_6$,
$M/2.5$		$M/2.5$ and $M/2.5$. Conc. ratio n = 1 : 1.		
20	0	17.8	17.80	$K_2UO_2FeCy_6$, $0.12UO_2(NO_3)_2$
18	2	17.0	18.88	$K_2UO_2FeCy_6$, $0.059UO_2(NO_3)_2$
16	4	16.1	20.12	$K_2UO_2FeCy_6$.

It is observed from the above tables that in direct thermometric titrations with aqueous solution, the observed titre value of uranyl nitrate is 25 c.c. which is higher than the calculated titre 21.48 c.c., but in alcoholic solution, the observed titre value

approaches the calculated one for the compound $K_2UO_2FeCy_6$. In the reverse titrations 20 c.c. of uranyl nitrate = 16 c.c. of K_4FeCy_6 which is lower than the calculated value 18.6 c.c. In this case also by the addition of alcohol, the observed value gradually rises to approach the calculated titre 18.6. On the basis of these observations the thermometric titrations indicate the formation of the compound $K_2UO_2FeCy_6, xUO_2(NO_3)_2$. In concentrated solutions there is a marked tendency for the formation of the compound $K_2UO_2FeCy_6$. Similar results have also been obtained by conductometric and potentiometric titrations. The slight discrepancy between the observed and calculated amounts of the one reactant required for 20 c.c. of the other arises from the hydrolytic nature of these compounds as well as adsorption effects. In our previous communications on the composition of metallic ferrocyanides the reasons for the discrepancy have been explained. Due to the tendency of uranyl ferrocyanide to hydrolyse in aqueous solution more uranyl nitrate than its calculated equivalent should be required when the latter is added to potassium ferrocyanide (direct titration) and the reverse will be the case when potassium ferrocyanide is added to uranyl nitrate (reverse titration). This effect will be minimised in aqueous alcoholic solutions and this is what has been observed. The adsorption effects of UO_2^{2+} and $FeCy_6^{4-}$ play their roles simultaneously with the hydrolysis and adsorption suffered by the precipitate during the titration.

FIG. 1



A/1-$UO_2(NO_3)_2$ *added* (c..c).

Comparing the results obtained by conductometric, potentiometric and thermometric titrations, clear evidence is obtained of the formation of a compound of the type $K_2UO_2FeCy_6$, $xUO_2(NO_3)_2$ when potassium ferrcoyanide is added to uranyl nitrate and *vice versa*. It appears that UO_2^{2+} are much more adsorbed than the $FeCy_6^{4-}$ during the precipitation of uranyl ferrocyanide. The formation of $K_2UO_2FeCy_6$ has also been supported by the quantitative analysis of the samples of uranyl ferrocyanide.

Experiments are in progress to study the hydrolysis of this compound and its adsorptive property.

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MANNICH BASES. PART I

By T. N. Ghosh and Saktipada Dutta

The synthesis of [α-N-(*o*-carboxy-benzamido)-β-phenyl]-ethylmethyl ketone and Mannich bases therefrom is described.

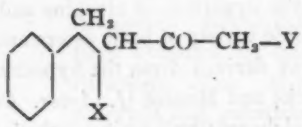
In the search for synthetic antispasmodics having both a neurotropic and musculotropic action in one molecule, the structures of atropine and papaverine have served as patterns for the preparation of a wide variety of basic esters and amines. Some of these compounds may be considered as derived from the hypothetical cleavage of tropine or papaverine. As for example, Blicke and Monroe (*J. Amer. Chem. Soc.*, 1939, **61**, 91) have synthesised methyldi-(β-*cyclo*hexylethyl)-amine, which has proved to be a strong antispasmodic. Although this compound is different from papaverine in structure, nevertheless, a relationship between its constitution and that of a completely hydrogenated papaverine can be established, if the *iso*quinoline ring is considered to be ruptured.

In recent years some simple *iso*quinoline derivatives, e.g., 3-methyl*iso*quinolines (Kreitmair, *Arch. Exp. Path. Pharm.*, 1932, **164**, 509 ; B.P. 488, 423) and 6:7-diethoxy-3-methyl-1-phenyl*iso*quinoline, have been found to be effective antispasmodics of low toxicity. Since substituted β-aminoketones have been found to possess appreciable antispasmodic activity (Denton *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 2048), it has been considered to be of interest to synthesise some substituted β-aminoketones, which may be considered as cleavage products of an *iso*quinoline ring system.

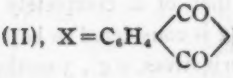
McPhee and Klingsberg (*ibid.*, 1944, **66**, 1134) have observed, without, however, furnishing any experimental detail, that chlorination of β-phenylethylmethyl ketone by gaseous chlorine produces mixtures. However, it has now been found that chlorination of this ketone under controlled conditions, as described in the Experimental, furnishes (α-chloro-β-phenyl)-ethylmethyl ketone (I) as a liquid (b.p. 142°-145°/5mm.) and the simultaneous formation of the isomeric chloromethyl-β-phenylethyl ketone could not be detected. Reference may be made, in this connection, to the sole formation of 1-acetoxy-3-chloro-4-pentanone by chlorination of 1-acetoxy-4-pentanone under such controlled conditions (Gravin, *J. Appl. Chem., U.S.S.R.*, 1943, **16**, 105; *Chem. Abst.*, 1944, **38**, 1239). The constitution of (I) has been proved by preparing, according to the unambiguous method of McPhee and Klingsberg (*loc. cit.*), (α-chloro-β-phenyl)ethylmethyl ketone (b.p. 139°-142°/5mm., as found in our hands), the 2:4-dinitrophenylhydrazone of which has been found to be identical with that of (I).

The condensation of the chloroketone (I) with potassium phthalimide has been studied under different conditions. When the condensation was attempted at 140°-150° in absence of any solvent (cf. Gabriel and Kroseberg, *Ber.*, 1889, **22**, 426), the reaction became vigorous with the formation of a much tarry matter. The use of anhydrous benzene or ethanol was found unsuitable for this purpose. Further work has shown that anhydrous acetone (cf. Elderfield and Werble, unpublished work; Elderfield, "Heterocyclic Compounds", Vol. 4, 1952, p. 338) is a more satisfactory solvent for effecting

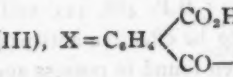
this condensation to yield (α-phthalimido-β-phenyl)-ethylmethyl ketone (II) in the form of a dark, heavy liquid. This crude product has been straightaway hydrolysed by caustic soda (cf. Haworth, Perkin and Pink, *J. Chem. Soc.*, 1925, 1708) to [α-N-(*o*-carboxybenzamido)-β-phenyl]-ethylmethyl ketone (III) which responds to the Mannich reaction with paraformaldehyde and a secondary amine to furnish (IV), characterised as *picrate*. It is significant to note that, during heating to effect the Mannich reaction, the intermediate carboxy compound undegoes ring-closure to yield the imide (IV). This is reminiscent of the facile conversion of allylphthalamic acid to N-allylphthalimide in boiling methyl alcohol (Carrara, *Gezzetta*, 1949, **79**, 834) and similar other instances.



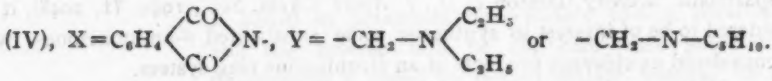
(I), X=Cl; Y=H.



(II), X=C$_6$H$_4$<CO>N-; Y=H.



(III), X=C$_6$H$_4$<CO$_2$H, CO—NH->; Y=H.



(IV), X=C$_6$H$_4$<CO>N-, Y= $-CH_2-N<C_2H_5, C_2H_5$ or $-CH_2-N-C_5H_{10}$.

The compound (III) could not be induced to yield an *iso*quinoline derivative by the Bischler-Napieralski reaction. This cyclisation might be possible through the ester of (III) (cf. Haworth *et al.*, *loc. cit.*) and work on this aspect would be undertaken in due course.

EXPERIMENTAL

(α-Chloro-β-phenyl)-ethylmethyl Ketone (I).—To an ice-cooled solution of β-phenylethylmethyl ketone (28 g.) in anhydrous chloroform, dry chlorine gas was slowly passed till the increase in weight was about 9.8 g. After removal of chloroform under reduced pressure, the residue was treated with cold water, when a heavy oil separated. The oil was extracted with ether and the ethereal layer washed twice with water and then dried over anhydrous sodium sulphate. After removal of ether, the oil (30 g.) was distilled under reduced pressure, b.p. 142°-145°/5mm., yield 27 g. (Found : Cl, 19.82. $C_{10}H_{11}OCl$ requires Cl, 19.45 per cent).

The 2:4- *Dinitrophenylhydrazone*, prepared according to the method of Shriner and Fuson ("The Systematic Identification of Organic Compounds", 1948, p. 171), was once crystallised from a mixture of chloroform and petroleum ether (b.p. 60°-80°) and melted at 137-38°. (Found: N, 15.28. $C_{16}H_{15}O_4N_4Cl$ requires N, 15.44 per cent). A sample of

2:4-dinitrophenylhydrazone, similarly prepared from (α-chloro-β-phenyl)-ethylmethyl ketone (McPhee and Klingsberg, *loc. cit.*), melted at 137-38° (lit., 138.5-139.5°) and showed no depression when mixed with the above sample.

(α-Phthalimido-β phenyl)-ethylmethyl Ketone (II).—A mixture of the above compound (I, 30 g.), potassium phthalimide (35 g.) and anhydrous acetone (100 c.c.) was heated under reflux on the water-bath for 24 hours. After the reaction was over, the dark coloured mixture was cooled in ice and then filtered. The solid was twice washed with anhydrous acetone and found to be a mixture (7 g.) of phthalimide and potassium chloride.

The washings and the filtrate were mixed together and after removal of acetone, a viscous mass was left behind. In view of phthalimide being insoluble in benzene, this viscous mass was treated with anhydrous benzene (75 c.c.), when there was a further separation of a small quantity of phthalimide (1.5 g.), which was filtered. Removal of benzene from the filtrate left the crude product (II) as a dark, heavy liquid (50 g.), which was straightaway hydrolysed as described below.

[α-N-(o-Carboxy-benzamido)-β-phenyl]-ethylmethyl Ketone (III).—A mixture of the above crude product (II, 50 g.) and an aqueous caustic soda solution (10%, 70 c.c.) was heated under mild reflux for one and one-half hours and then cooled. A small quantity of an oily layer which was left behind was extracted with ether and the alkaline solution treated with Nuchar and then filtered. On acidification with concentrated hydrochloric acid, a gummy mass separated, which on scratching solidified. The solid was purified by solution in aqueous sodium bicarbonate and acidification with concentrated hydrochloric acid. It was crystallised from warm aqueous ethanol in cream-coloured rectangular plates (22 g.), m.p. 140-42° (unaltered by further crystallisation). (Found: N, 4.38; neut. equiv., 308.8. $C_{18}H_{17}O_4N$ requires N, 4.50 per cent; neut. equiv., 311).

The *semicarbazone* was crystallised from ethanol in colorless needles, m.p. 177-78°. (Found: N, 15.04. $C_{19}H_{20}O_4N_4$ requires N, 15.21 per cent). It is soluble in aqueous sodium bicarbonate.

In order to cyclise the above compound (III) to an *iso*quinoline derivative, it was treated with phosphorus oxychloride in presence of anhydrous toluene, and the mixture was heated in an oil-bath at 120° for 2 hours. The cooled mixture was poured into crushed ice. From the aqueous layer no basic compound could be isolated and the toluene layer furnished an intractable tar.

1-Diethylamino-4-phthalimido-5-phenylpentan-3-one (IV ; Y=diethylaminomethyl).—A mixture of the above compound (III, 4 g.), diethylamine hydrochloride (2.3 g.), paraformaldehyde (0.5 g.) and anhydrous ethanol (40 c.c.) was heated under reflux for 2 hours. The solution gradually turned red and after addition of a further quantity of paraformaldehyde (0.3 g.) the mixture was heated under reflux for another 2 hours. After distillation of 30 c.c. of ethanol under reduced pressure, the residue was poured into an excess of anhydrous ether, when the hydrochloride (4.5 g.) was deposited as a brownish solid. The hydrochloride, which was found to be somewhat hygroscopic, yielded on treatment with excess of ammonium hydroxide a pasty mass, readily soluble in dilute hydrochloric acid but insoluble in aqueous sodium bicarbonate and also in cold dilute alkali. This base could not be obtained in a pure condition.

The *picrate* was obtained from an ethanolic solution of the hydrochloride as yellow needles, melting at 156-58° to a dark viscous mass. (Found: N, 11.27. $C_{22}H_{26}O_3N_2$, $C_6H_3O_7N_3$ requires N, 11.53 per cent).

1-*Piperidino-4-phthalimido-5-phenylpentan-3-one* (IV, Y=piperidinomethyl).—The hydrochloride was similarly prepared and found to be hygroscopic. The free base which was obtained as a pasty mass did not solidify on long standing *in vacuo*. It is readily soluble in dilute hydrochloric acid and insoluble in cold dilute alkali.

The *picrate* was obtained from ethanol as yellow needles, melting at 151-53° to a dark viscous mass. (Found: N, 11.57. $C_{24}H_{26}O_3N_2$, $C_6H_3O_7N_3$ requires N, 11.30 per cent).

Sincere thanks of the authors are due to Dr. U. P. Basu, for his kind interest in this investigation.

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SEARCH FOR NEW ANTISPASMODICS. PART V*

By T. N. GHOSH AND SAKTIPADA DUTTA

α-Acetamido-β-diethylamino(or piperidino)-propiophenone, on reduction with aluminium *iso*propoxide, furnishes a compound which appears to be an oxazoline derivative (III). Condensation of diethylaminoacetone with benzaldehyde in alkaline medium yields simultaneously ω-diethylaminobenzalacetone (IV) and ω-hydroxybenzalacetone. (IV) has been reduced catalytically to ω-diethylaminobenzylacetone (VII).

The observation that certain substituted β-aminoalkyl-arylketones exhibit antispasmodic action (cf. Blicke, *Ann. Rev. Biochem.*, 1944, **13**, 549) has led Denton *et al.* (*J. Amer. Chem. Soc.*, 1949, **71**, 2048) to synthesise a number of β-aminoketones of the general structure: R-CO-CH (R′)-CH_2-Am (where R is an aryl or heterocyclic group, R′ is a hydrogen or phenyl group and Am is a substituted amino group). Some of these compounds have equalled β-diethylaminoethyldiphenyl acetate hydrochloride (Trasentin) in antispasmodic action. Subsequently Denton, Lawson, Neier and Turner (*ibid.*, 1949, **71**, 2050) have converted these ketones into tertiary alcohols and have observed that these tertiary alcohols, in general, show greater antispasmodic activity than the ketones from which they have been derived. This observation is reminiscent of the structure of adrenaline, which contains a secondary alcoholic group.

In view of the above observations, it has been considered desirable to synthesise, as possible antispasmodics, some ketones and secondary alcohols containing tertiary amino groups, and the preliminary work, so far carried out in this direction, is recorded in this communication.

In a previous communication (Ray Chaudhuri and Ghosh, this *Journal*, 1951, **28**, 566) the synthesis of α-acetamido-β-diethylamino (or piperidino)-propiophenone (I) has

* A preliminary note on the subject was published in the *Science and Culture*, 1953, **18**, 441.

been reported and it has been observed that compounds of this type possess some antispasmodic action. The reduction of this ketone (I) to the corresponding secondary alcohol has now been attempted with two objects in view: first to study the antispasmodic activity of the corresponding secondary alcohol and secondly, to subject the secondary alcohol, if formed, to the Bischler-Napieralski reaction to furnish an *iso*quinoline derivative containing a tertiary amino group. However, (I) has been found to yield, after reduction with aluminium *iso*propoxide, a compound which appears to be the oxazoline derivative (III), evidently formed from the intermediate secondary alcohol (II). The oxazoline structure is based on analytical figures and on the observation that the substance does not yield any benzoate, *p*-nitrol nzoate or acetate.

(II) (III)

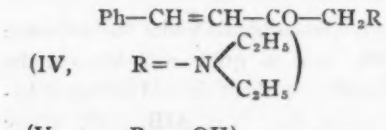
(R = piperidino or diethylamino)

Although the formation of oxazolines from *N*-acylaminocarbinols under the influence of a dehydrating agent (Krabbe *et al.*, *Ber.*, 1940, **73B**, 656) is quite well known, the formation of such oxazolines from β-hydroxyalkylamides, without the aid of any dehydrating agent, has also been previously reported (Dersin, *Ber.*, 1921, **54B**, 3158; Wiley and Bennett, *Chem. Rev.*, 1949, **44**, 453). In fact, alkylolamides have been converted into oxazolines by heating, in the absence of dehydrating agents, in a high boiling solvent like toluene or xylene (U. S. Patent, 2,416, 552; *Chem. Abs.*, 1947, **41**, 3823).

A symmetrical ketone, such as acetone, condenses with one mole of benzaldehyde in only one way to form benzalacetone. On the other hand, it is possible for an unsymmetrical ketone, such as phenylacetone or methylethyl ketone, to condense with one mole of benzaldehyde to yield two isomeric ketones. Goldschmidt and his co-workers (*Monatsh*, 1897, **18**, 437; 1898, **19**, 406; 1901, **22**, 657) studied the reaction between phenylacetone and benzaldehyde and reported that in acid medium stibylmethyl ketone was formed. Harries and Müller (*Ber.*, 1902, **35**, 966) reported that benzaldehyde condensed with methylethyl ketone in presence of sodium hydroxide, forming benzylidene-methylethyl ketone, whereas in presence of hydrogen chloride, γ-benzylidene-ethyl-methyl ketone was formed. Similarly, interaction of nitroacetone with one mole of benzaldehyde in alkaline medium leads to the formation of ω-nitrobenzalacetone (Harries, *Annalen*, 1901, **319**, 254). It therefore appears that under base-catalysed condition such a condensation occurs at the methyl carbon, whereas under acid-catalysed condition the reaction takes place at the methylene carbon. The condensation of diethylaminoacetone (Stoermer and Dzimiski, *Ber.*, 1895, **28**, 2256) with benzaldehyde in alkaline medium has now been found to lead to the formation of two compounds, one non-basic solid, devoid of nitrogen and the other is a heavy liquid possessing basic property. The former compound has been found to be ω-hydroxybenzalacetone (V), evidently

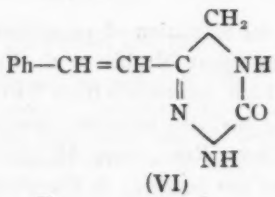
formed from the intermediate, ω-diethylaminobenzalacetone (IV), by hydrolysis in presence of alkali. The constitution of (V) follows from the observations that the compound yields β-naphthol on treatment with concentrated sulphuric acid, and furnishes the triazine (VI) when reacted with semicarbazide hydrochloride in presence of sodium acetate. On oxidation with alkali permanganate, (V) yields benzoic acid. The above heavy liquid, which, however, could not be distilled without decomposition, has been characterised as (IV) by the formation of semicarbazone, and yields (V) on hydrolysis with alkali. The possibility of the above reaction with benzaldehyde having taken place at the methylene carbon is ruled out on the ground that the condensation product, so formed, would lead, on similar hydrolysis in presence of alkali, to the formation of methylbenzylglyoxal, a compound which is ascribed by Moureu (*Compt. rend.*, 1928, **186**, 380, 503) to exist in two forms: CH_3-CO-CO-CH_2Ph and CH_3-CO-C (OH)=CHPh, one being a liquid (b.p. 104°/10 mm.) and the other, a solid (m.p. 69-70°).

(IV) has been straight away reduced catalytically over palladium-charcoal to yield (VII). The base (VII), even after distillation under reduced pressure, was somewhat dark coloured and it was not found possible to remove the colour by a second distillation. It gives a hygroscopic hydrochloride and has been characterised by the formation of picrate and 2:4-dinitrophenylhydrazone.

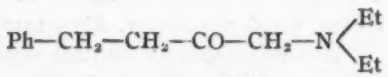


(IV, R = $-N(C_2H_5)_2$)

(V, R = −OH)



(VI)



(VII)

EXPERIMENTAL

2-Methyl-4-piperidinomethyl-5-phenyl-2-oxazoline (III, R=piperidino).—Aluminium *iso*propoxide was prepared by treating aluminium foil (3.5 g.) with a mixture of dry *iso*propyl alcohol (40 c.c.), mercuric chloride (0.4 g.) and carbon tetrachloride (1 c. c.).

To the above mixture, heated in an oil-bath at 100° under reflux, a solution of α-acetamido-β-piperidino-propiophenone (11 g., Ray Chaudhuri and Ghosh, *loc. cit.*) in dry *iso*propyl alcohol (110 c.c.) was added dropwise during 1 hour. After addition was over, the mixture was refluxed for 2 hours, concentrated at 110°-115° to half its volume to remove acetone (the presence of which was confirmed) and made up to its original volume with *iso*propyl alcohol. This process without alteration was repeated three more times. The solution of *iso*propyl alcohol was then concentrated to half its volume and the residual *iso*propyl alcohol was distilled off under reduced pressure. The residue was cooled and treated with an excess of cold, dilute hydrochloric acid (5%), when a slight heat was generated. After thorough trituration the mixture was filtered and the filtrate

basified, under cooling, with ammonium hydroxide. The gelatinous precipitate was filtered, thoroughly washed with water and extracted with boiling ethanol. The distillation of the ethanolic extract left a pasty solid which was purified by hydrochloric acid-ammonium hydroxide treatment and was crystallised from benzene-ethanol mixture in brownish needles, melting at 187-88° to a dark viscous mass. (Found: C, 73.82; H, 8.18; N, 10.37. $C_{16}H_{22}ON_2$ requires C, 74.41; H, 8.52; N, 10.85 per cent). Even though the compound was heated with an excess of benzoyl chloride in pyridine solution at 100° in an oil-bath for 4 hours, no benzoate was formed. Under similar conditions, there was no formation of any *p*-nitrobenzoate or acetate.

The *picrate* was obtained by adding an ethanolic solution of picric acid to an ethanolic solution of the substance, when a yellow solid was immediately precipitated. It was crystallised from acetone-benzene mixture in yellow needles, melting at 193-94° (decomp.) to a dark viscous mass. (Found: N, 14.0. $C_{16}H_{22}ON_2,C_6H_3O_7N_3$ requires N, 14.3 per cent).

2-Methyl-4-diethylaminomethyl-5-phenyl-2-oxazoline (III, R=diethylamino) was similarly prepared as the previous compound (III, R=piperidino) and was crystallised from ethanol-ether mixture in brownish needles, melting at 181-83° to a dark viscous mass. (Found: N, 11.64. $C_{15}H_{22}ON_2$ requires N, 11.38 per cent).

The *picrate* was crystallised from acetone-benzene mixture in yellow needles, melting at 190-91° (decomp.) to a dark viscous mass. (Found: N, 14.95. $C_{15}H_{22}ON_2$, $C_6H_3O_7N_3$ requires N, 14.73 per cent).

Condensation of Diethylaminoacetone with Benzaldehyde: Formation of ω-Diethylaminobenzalacetone (IV) *and ω-Hydroxybenzalacetone* (V).—To an ice-cooled mixture of benzaldehyde (51 g.), caustic soda solution (10%, 200 c.c.) and ethanol (95%, 100 c. c.), diethylaminoacetone (Stoermer and Dzimiski, *loc. cit.*, 60 g.) was gradually added with shaking during 30 minutes. The mixture, cooled in ice, was stirred for 2 hours and then kept in the refrigerator for about 30 hours. Two distinct layers separated: the upper layer was separated and the lower aqueous layer rejected. The upper layer was mixed with benzene and the solution was thrice extracted with cold 10% hydrochloric acid to remove the basic compound. The residual benzene solution soon deposited a white flaky solid (V, 15 g.), which was filtered and twice crystallised from ethanol in colorless needles, m.p. 170-72°. (Found: C, 73.51; H, 5.78. $C_{10}H_{10}O_2$ requires C, 74.07; H, 6.17 per cent).

The above hydrochloric acid extracts were mixed together, stirred with Nuchar (5 g.) and filtered. The filtrate, cooled in ice, was basified with dilute caustic soda solution and the heavy liquid was extracted with ether. The distillation of ether left a dark, heavy liquid (IV, 20 g.) which showed tendency to decompose when distillation under reduced pressure was attempted. It furnished a *semicarbazone*, crystallising from aqueous ethanol in brownish rectangular plates, m.p. 122-23°. It was dried *in vacuo* at 65°-70° over P_2O_5. (Found: N, 20.05. $C_{18}H_{22}ON_4$ requires N, 20.43 per cent).

Treatment of ω-Diethylaminobenzalacetone (IV) *with alkali: Formation of ω-Hydroxybenzalacetone* (V).—An ice-cooled solution of caustic soda (4 g.) in a mixture of water (40 c.c.) and ethanol (95%, 20 c.c.) was added slowly to the compound (IV, 13 g.) and the mixture was occasionally shaken in an ice-bath for 4 hours, and then

allowed to stand at room temperature for 36 hours with occasional shaking. After keeping in the refrigerator for 36 hours more, the mixture was extracted with ether and the ethereal layer separated and washed twice with 10% cold hydrochloric acid. Removal of ether left a sticky solid, which was triturated with benzene and then finally crystallised from ethanol in colorless needles (6.5 g.), m.p. 170-72°. Admixture with the above sample of (V) produced no depression in m.p.

Conversion of ω-Hydroxybenzalacetone into β-Naphthol.—To an ice-cooled mixture of ω-hydroxybenzalacetone (2 g.) and glacial acetic acid (30 c.c.), concentrated sulphuric acid (10 c.c.) was gradually added and the mixture kept in the refrigerator for about 12 hours. After heating the mixture for 30 minutes on the water-bath, it was cooled and the insoluble solid filtered. The filtrate was neutralised with sodium carbonate and then extracted with ether. The ether extract was washed with water and left, after distillation, a brown solid (0.6 g.), crystallising from boiling water in cream coloured leaflets, m.p. 122-23° (mixed m.p. with a sample of β-naphthol being undepressed). It gave a diazo reaction with a mixture of aniline hydrochloride and sodium nitrite.

The above insoluble solid was triturated with cold dilute caustic soda solution and filtered. The filtrate was acidified with dilute hydrochloric acid and the mixture extracted with ether. The ethereal solution yielded a further quantity of crude β-naphthol (0.1 g.). The solid residue, after purification, was found to be the original compound (V).

Oxidation of ω-Hydroxybenzalacetone with alkaline Potassium Permanganate.—A mixture of the compound (V, 1 g.), potassium permanganate (1.5 g.) and caustic potash (0.2 g.) in water (30 c.c.) was heated under reflux on the wire gauze till the solution was practically decolorised. The mixture, after treatment with Nuchar (0.1 g.), was filtered, and the filtrate acidified, under cooling, with concentrated hydrochloric acid. The solid separating was crystallised from water in colorless needles, m.p. 119-20° (mixed m.p. with a sample of benzoic acid being undepressed).

3-Keto-6-cinnamyl-2:3:4:5-tetrahydro-1:2:4-triazine (VI).—To a solution of the compound (V, 2 g.) in ethanol (60 c.c.), a mixture of semicarbazide hydrochloride (4 g.), sodium acetate (6 g.) and water (15 c.c.) was added and the resulting mixture was heated under reflux for about 15-20 minutes, when a crystalline solid separated out. It was filtered, washed with water and crystallised from a large volume of ethanol in colorless rectangular plates, m.p. 227-28°. (Found: N, 21.02. $C_{11}H_{11}ON_3$ requires N, 20.89 per cent).

ω-Diethylaminobenzylacetone (VII).—To a solution of the compound (IV, 11g.) in ethanol (30 c.c.), palladium-charcoal (10%, 2 g.) was added and the mixture was shaken with hydrogen at room temperature under atmospheric pressure, when one equivalent of hydrogen was gradually absorbed and further absorption of hydrogen practically stopped. The catalyst was removed by filtration and washed with ethanol. The filtrate and washings were combined and the removal of ethanol under reduced pressure left a dark, mobile liquid. It distilled at 145°-150°/6-7mm. and although a second distillation was carried out, the distillate still retained a somewhat dark colour, and the colour deepened on standing.

The *picrate*, which was obtained by adding an excess of aqueous picric acid solution to a solution of the above compound in just the requisite quantity of dilute hydrochloric acid, was crystallised from ethanol-benzene mixture in yellow rectangular plates, m.p. 106-107°. (Found: N, 12.1. $C_{14}H_{21}ON$, $C_6H_3O_7N_3$ requires N, 12.5 per cent).

The 2:4-*dinitrophenylhydrazone* was crystallised from ethanol in orange-yellow plates, m.p. 218-20°. (Found: N, 17.18. $C_{20}H_{25}O_4N_5$ requires N, 17.54 per cent).

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INTERFACIAL TENSION AND COMPLEX FORMATION. PART I. SYSTEM : $HgBr_2$—NaBr—H_2O

By Miss Hemlata J. Kazi and C. M. Desai

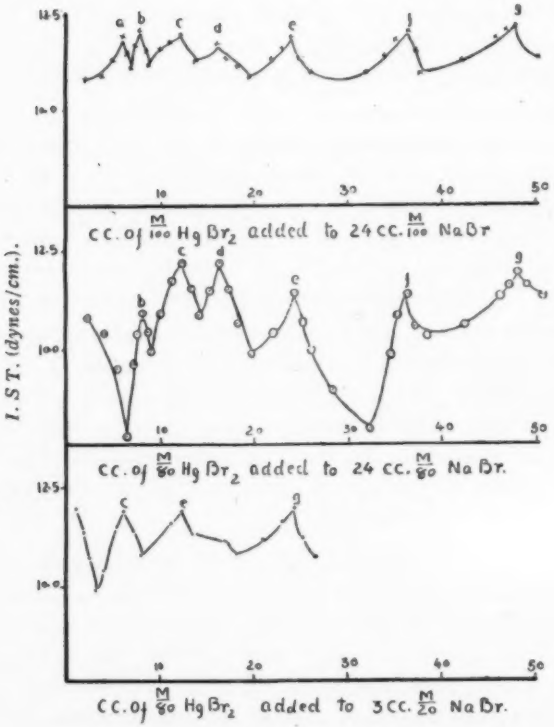
The results obtained with this system show the formation of only three, six and seven complexes with decreasing concentration of $HgBr_2$.

In mercuric bromide and potassium and ammonium bromide systems, three, six and seven complexes have been shown to exist in solution, as concentrations of both the salts in mixed solution are decreased progressively (unpublished). In this communication the results obtained with the sodium bromide system are reproduced.

Experimental

Three series of mixed solutions of both the salts of standard quality were prepared by the method of monovariation :

Fig. 1



(*a*) 4 NaBr. $HgBr_2$. (*b*) 3 NaBr. $HgBr_2$,
(*c*) 2 NaBr. $HgBr_2$. (*d*) 3 NaBr. 2 $HgBr_2$.
(*e*) NaBr. 2 $HgBr_2$. (*f*) 2 NaBr. 3 $HgBr_2$.
(*g*) NaBr. 2 HgBr.

(I) A requisite volume of mercuric bromide ($M/100$) was added to a measured volume of 42 c.c. of sodium bromide ($M/100$) in a 100 c.c. measuring flask and the total volume made up to 100 c.c. by addition of distilled water.

(II) A requisite volume of mercuric bromide ($M/80$) was added to 24 c.c. of sodium bromide ($M/80$) and the total volume made up to 100 c.c. in a 100 c.c. measuring flask.

(III) A requisite volume of mercuric bromide ($M/80$) was added to 3 c.c. of sodium bromide ($M/20$) and the total volume made up to 30 c.c. in a flask.

The details as regards the composition of the mixed solutions and the corresponding interfacial tension values of *n*-butyl acetate are shown in Fig. 1.

With decreasing concentrations of mercuric bromide and sodium bromide, three, six and seven complexes are found to appear in solution. However, it is interesting to observe that the formation of the complex $3NaBr.\ HgBr_2$ is preferentially favoured with the disappearance of the complex $4NaBr.\ HgBr_2$, when six complexes are formed as in the case of $HgCl_2$—NaCl—H_2O system (this *Journal*, 1953, **30**, 424).

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INTERFACIAL TENSION AND COMPLEX FORMATION. PART II. SYSTEM : $HgBr_2$—LiBr—H_2O

BY MISS HEMLATA J. KAZI AND C. M. DESAI

Only three and six complexes have been observed with decrease in the extent of salt concentrations in mixed solutions.

It has been previously shown that the potassium, ammonium and sodium bromide systems resemble the respective chloride systems in respect of complex formation. In this paper, the results of the lithium bromide system are reported.

EXPERIMENTAL

Two series of mixed solutions of both the salts of standard quality were prepared by the method of monovariation.

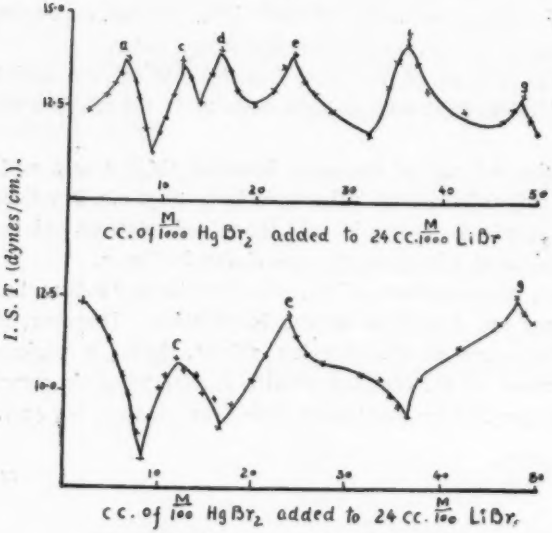
(I) A requisite volume of mercuric bromide ($M/1000$) was added to a measured volume of 24 c.c. of lithium bromide ($M/1000$) in a 100 c.c. measuring flask and the total volume made up to 100 c.c. by the addition of distilled water.

(II) Similarly, the series was prepared with mercuric bromide ($M/100$) and lithium bromide ($M/100$).

The details as regards the composition of mixed solutions and corresponding interfacial tension values of *n*-butyl acetate are shown in Fig. 1.

The results reveal the formation of only three and six complexes with progressive dilution of the mixed salt solution. The formation of the complex $3\ LiBr.\ HgBr_2$ is not favoured in spite of such determinations at a number of lower concentrations, viz.

FIG. 2



(*a*) $4LiBr.HgBr_2$. (*c*) $2LiBr.HgBr_2$.
(*d*) $3LiBr.2HgBr_2$. (*e*) $2LiBr.HgBr_2$.
(*f*) $2LiBr.HgBr_2$. (*g*) $LiBr.2HgBr_2$.

$M/4000$, $M/8000$ and $M/16000$ of both lithium and mercuric bromides. To obtain maximum number of complexes, dilution of the alkali salt solution should be progressively increased in the order : $Li > Na > K$. The extent of dilution is a measure of the magnitude of the binding force between the anions and the metal ions, which is in the order : $Li > Na > K$. This is in agreement with the increasing deformation effect of the cations in the order : $Li^+ > Na^+ > K^+$, in view of the greater polarising effect of the smaller cation (this *Journal*, 1953, **30**, 427), just as in the case of the chloride system.

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